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High-Efficiency Blue Photoluminescence in the $Cs_2NaInCl_6:Sb^{3+}$ Double Perovskite Phosphor

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Electronic Supporting Information

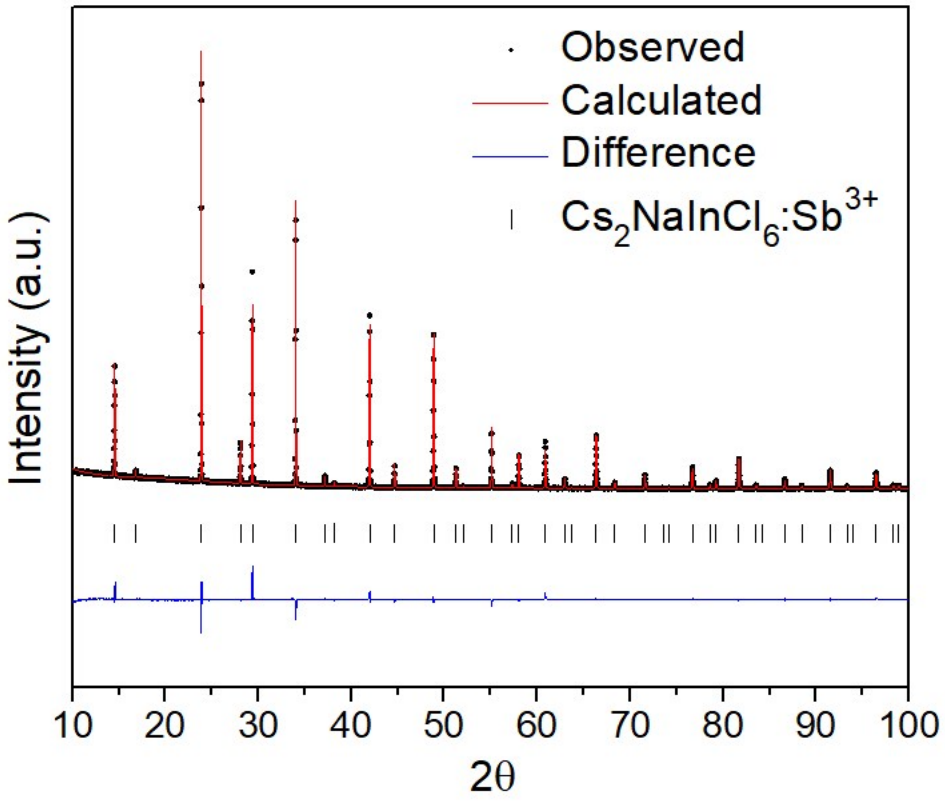

Figure S1. Rietveld refinement of sample (4). The observed data, calculated fit, and difference curve are shown with black dots, a red line, and a blue line, respectively.

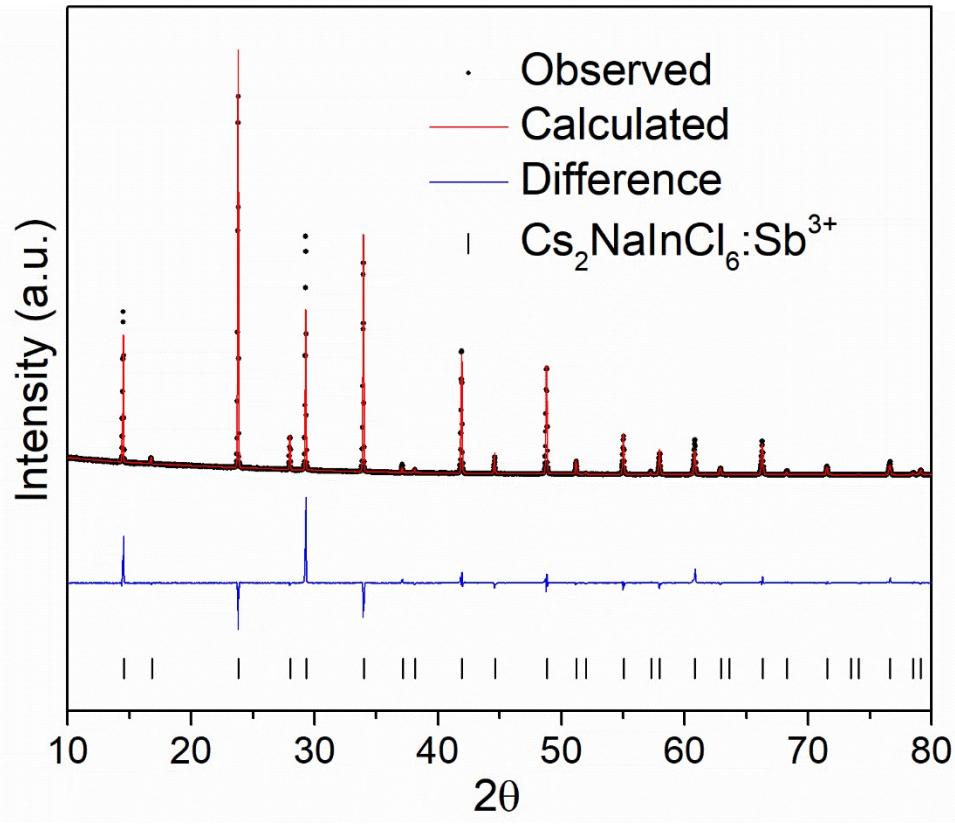

Figure S2. Rietveld refinement of sample (8). A phase pure material was observed, although minor strain broadening from the incorporation of Sb^{3+} was observed. The observed data, calculated fit, and difference curve are shown with black dots, a red line, and a blue line, respectively.

Table S1. Rietveld refinement results for $Cs_2NaInCl_6$.

Source	Cu Kα1 X-rays
Chemical formula	$Cs_2NaInCl_6$
Sample Number	1
Formula weight	616.34 g/mol
Temperature	298 K
Wavelength	1.5406 Å
Crystal system	Cubic
Space group	$Fm\bar{3}m$ (#225)
Unit Cell	
a	10.53344(4) Å
b	10.53344(4) Å
c	10.53344(4) Å
α	90°
β	90°
γ	90°
V (Å^3)	1168.721(1)
Z	4
*Atomic parameters**	
Cl x	0.2641(3)
Cs U_{iso} (Å^2)	0.0322
Na U_{iso} (Å^2)	0.0279
In U_{iso} (Å^2)	0.0184
Cl U_{iso} (Å^2)	0.0287
Refinement statistics	
d-space range	4.4359 – 0.7822 Å^{-1}
χ^2	1.750
R_p	5.73
R_{wp}	7.58

*The atoms sit on the following Wyckoff sites: Cs on 8c (¼,¼,¼), Na on 4a (0,0,0), In on 4b (½,½,½) and Cl on 24e (x,0,0).

All refinement statistics taken from: http://www.topas-academic.net/Technical_Reference.pdf, page 36. Accessed 12-11-2019.

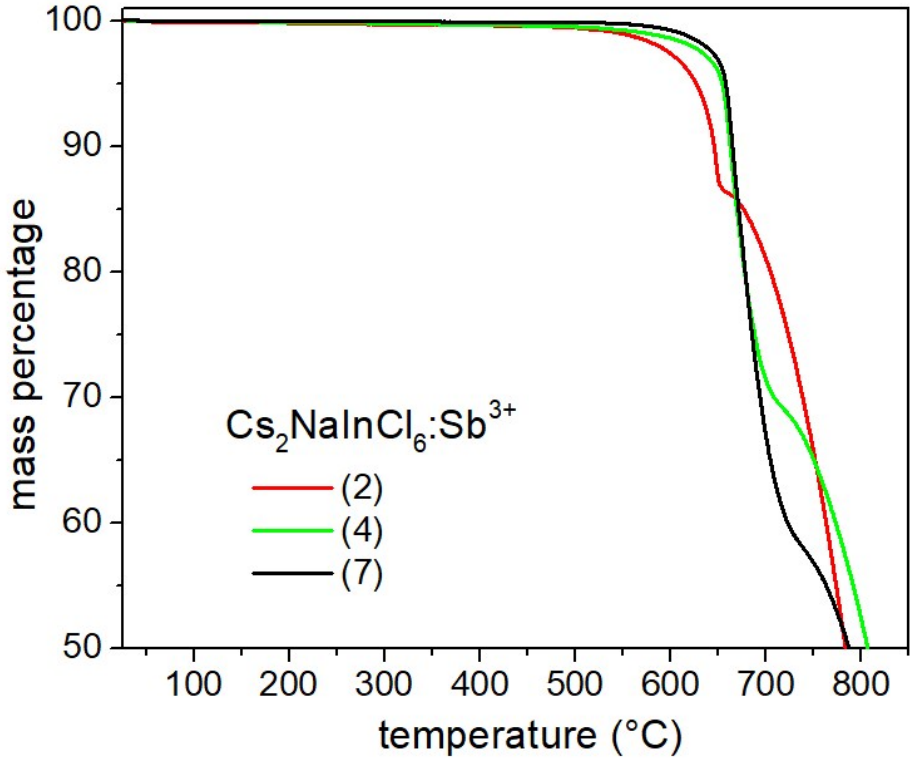

Figure S3. Thermogravimetric analysis of three $Cs_2NaInCl_6:Sb^{3+}$ samples.

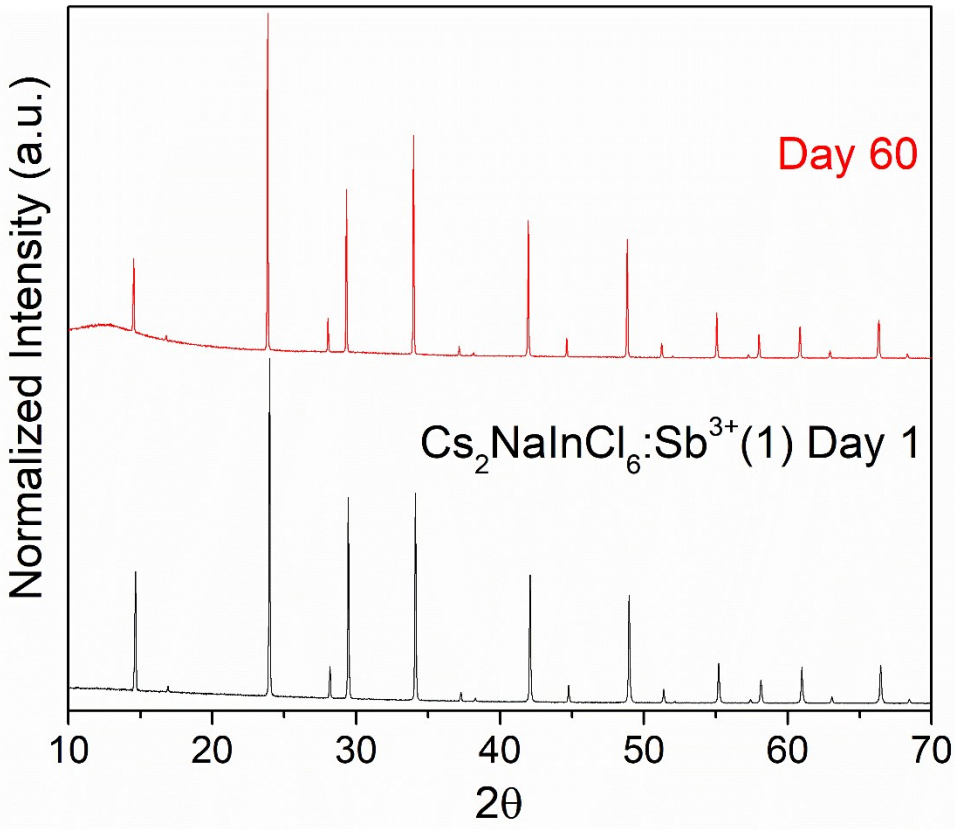

Figure S4. Stability of sample (1) via PXRD stored under ambient conditions, over the course of two months.

Table S2. PLQY for a dilute powder of sample (7) measured ~ 4 weeks apart. The sample was stored in air. The stability of the PLQY is the same within experimental error (± 5%).

Day	PLQY Average
1	37.5 %
35	42.9 %

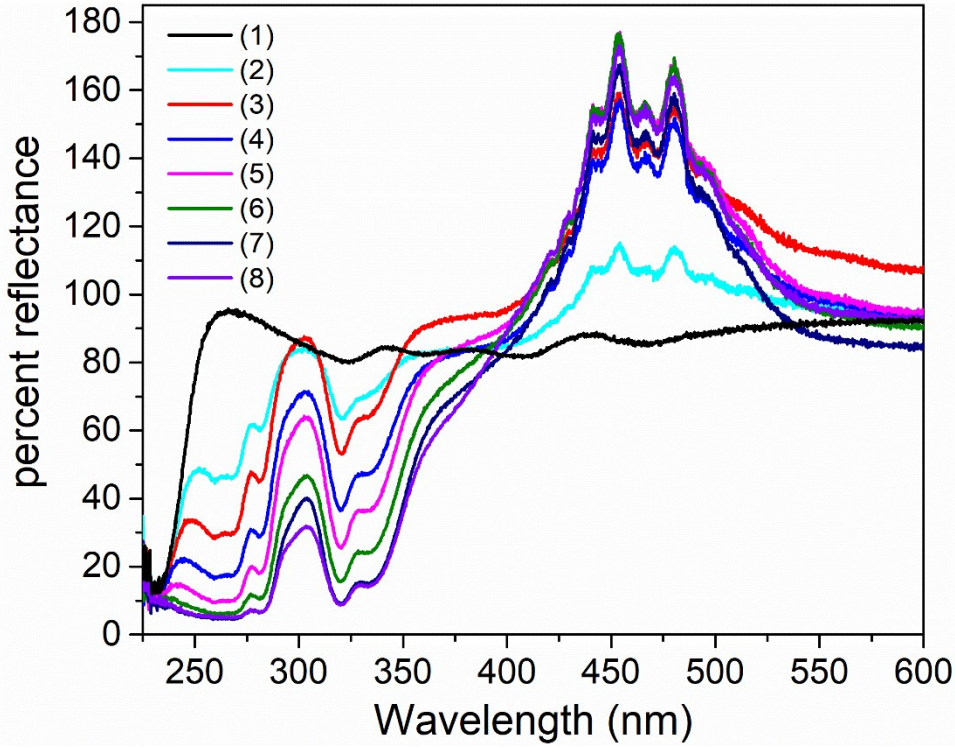

Figure S5. Diffuse reflectance spectra of $Cs_2NaInCl_6:Sb^{3+}$. The features near 450 nm where the reflectance exceeds 100% are indicative of photoluminescence.

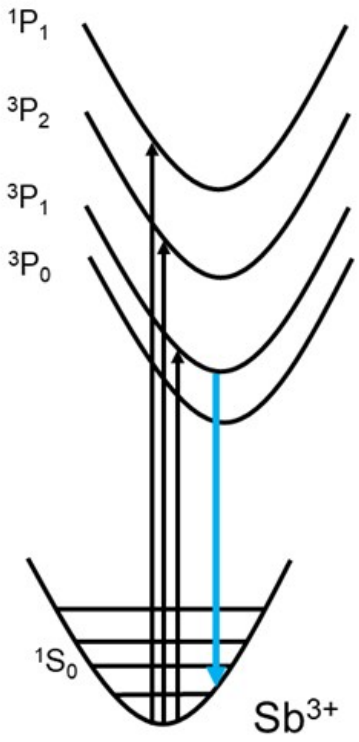

Figure S6. Optical transitions of a Sb^{3+} ion.

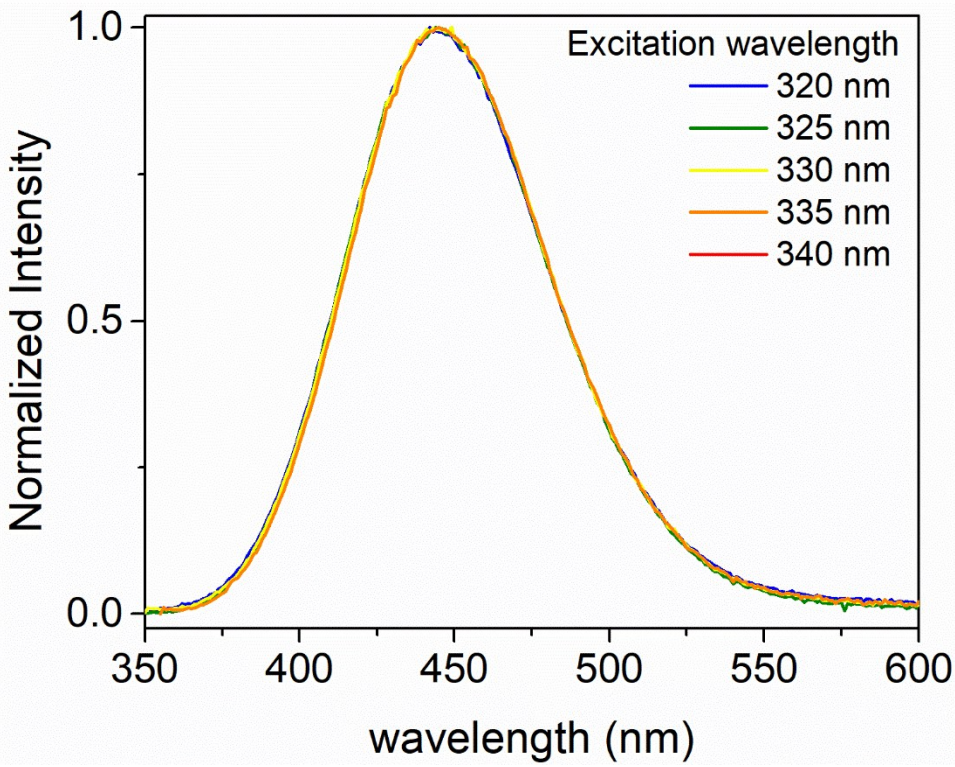

Figure S7. Emission profile when excited at various wavelengths.

Quantum Yield:

All photo-luminescent quantum yield (PLQY) measurements were performed using the Jovin Horiba FluoroMax4 fluorimeter equipped with the Quanta-φ F-3029 integrating sphere (15 cm), a PTFE blank stub as the sample holder, an R928 PMT detector, and a 150 W Xenon lamp.

The optimal phosphor concentration for signal linearity was determined by performing a dilution study. For the dilution experiments, the raw powder was diluted with a non-luminescing barium sulfate powder ($BaSO_4$, Wako, #022-00425, Lot SDF1291) in concentrations ranging from 100% to 10% by weight and the PLQY determined for each dilution. Dilutions were made until the PLQY value no longer showed a concentration dependence. The optimal concentration determined by this method was 10% (wt) of phosphor to $BaSO_4$.

For analysis, each sample was dried overnight in a 50°C vacuum oven and the powders mixed with an optically-clear, two-part silicone resin (Momentive, RTV615) at 22% (wt) of powder to resin. The powder was either the pure phosphor powder for low absorbance samples or a mixture of phosphor and $BaSO_4$ for highly absorbing samples. The samples were then homogenized in high-speed mixer (FlackTek Inc., DAC 150.1 FVZ-K) at 2500 RPMs for 5 min. A blank reference sample was prepared by the same method using only non-luminescing $BaSO_4$ as the encapsulated powder. To make three replicates, each sample mixture was deposited on a glass slide in three approximately equal drops. The drops were then degassed in a vacuum oven at room temperature for 10 mins followed by curing at 150 °C for 15 mins. After curing, the films were approximately 0.5 mm thick. Each of the three films were carefully peeled off the glass slide and cut into a 20 mm diameter discs for analysis. Each 20 mm diameter disc should contain approximately 30 mgs of powder.

For PLQY analysis, typical methods used a 0.1 sec integration time, a 0.25 nm increment for the absorbance region, and a 0.5 nm increment for the luminescence region. A bandpass of 2.75 nm was used for both excitation and emission slits. All samples and the blank were excited at 335 nm (λ_{max}) and the absorbance and luminescence signals integrated from 325 to 345 nm and 370 to 570 nm, respectively. When necessary, neutral density and long pass filters were used to attenuate the signal to appropriate levels and to reduce scattering. Radiometric (red) and dark count corrections were applied during data acquisition while sphere and filter corrections and integration time differences were applied in the final calculation of PLQY and chromaticity in in the FluorEssence™ analysis package for Quantum Yield (FluorEssence v3.8.0.60, Origin v8.6001) by the general formula below. The reported PLQY values are the average of the 3 replicates of each sample with standard deviation.

$$Quantum\ Yield = \left(\frac{Em_s - Em_b}{Ex_b - Ex_s} \right) * 100$$

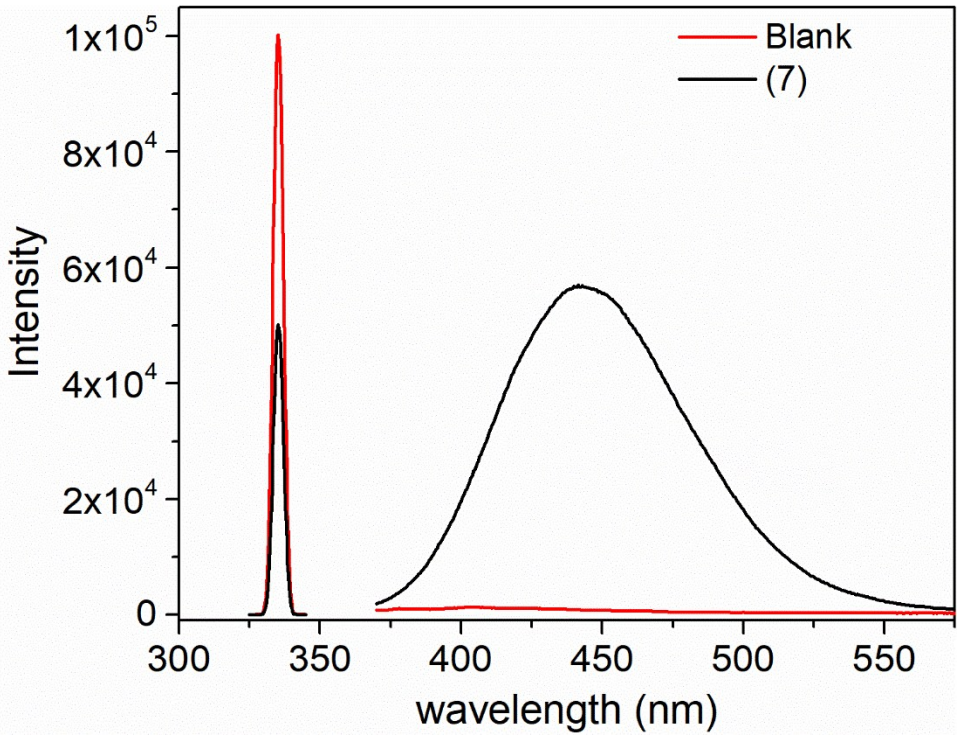

Figure S8. Quantum efficiency excitation and emission measurements of blank and sample (7).

Table S3. Results of quantum efficiency measurements

Sample	Average	Standard deviation
(6)	79.0 %	4.7
(7)	60.1 %	4.8

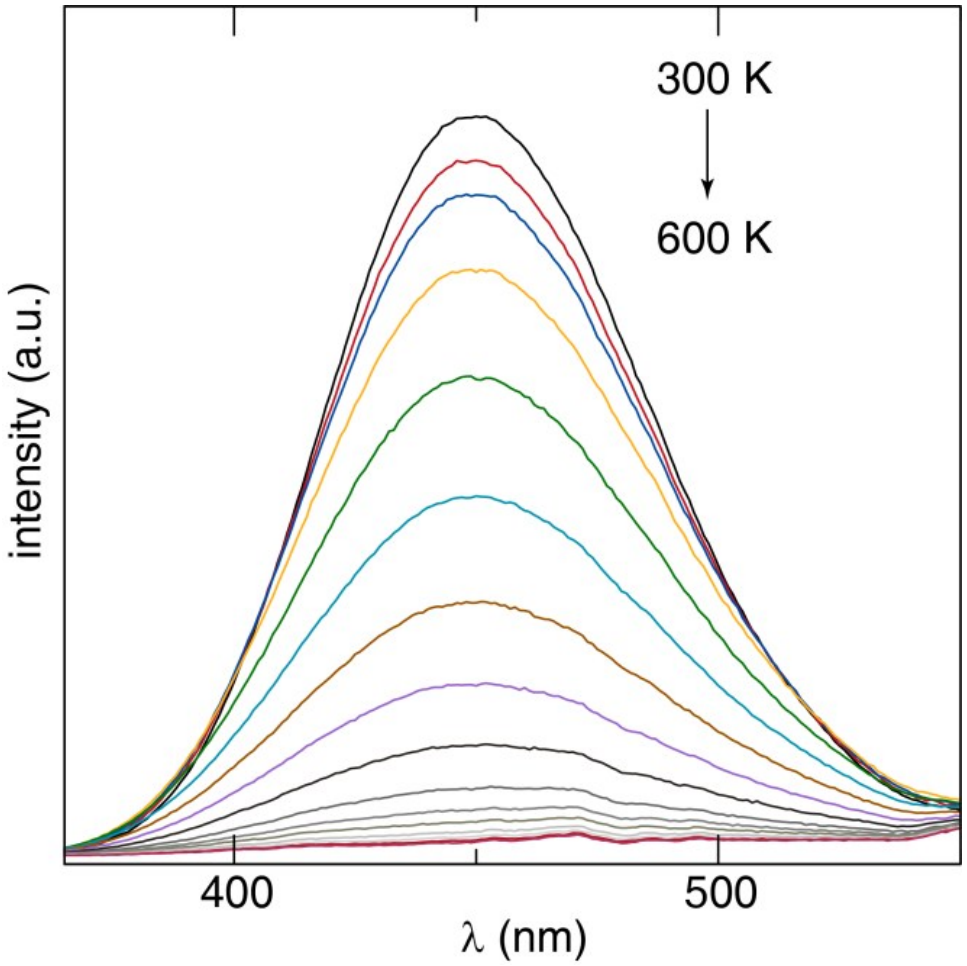

Figure S9. Emission spectra collected from 300 K to 600 K. The minimal shift of the emission maxima as a function of temperature indicates excellent color stability.

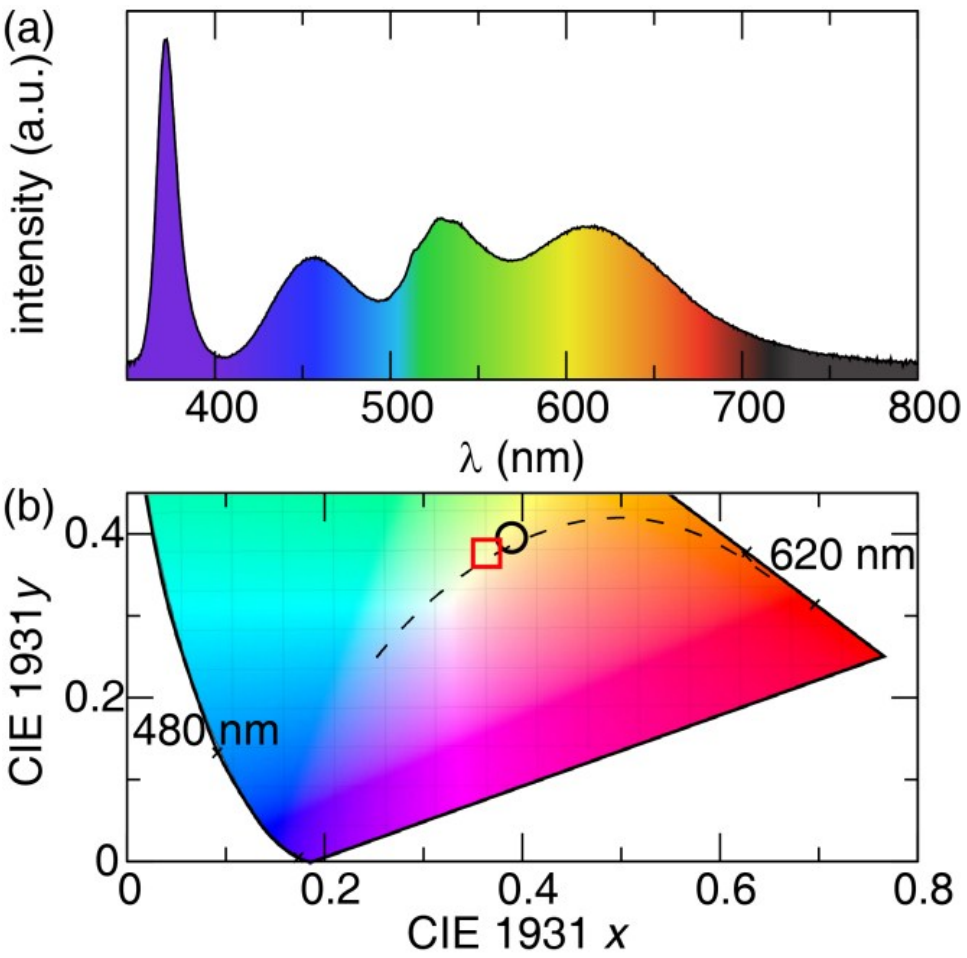

Figure S10. (a) The luminescence spectrum of a pc-LED composed of a near-UV LED (λ_{ex} = 370 nm), $BaMgAl_{10}O_{17}:Eu^{2+}$, $Sr_2Si_5N_8Eu:^{2+}$ and β-SiAlON:Eu^{2+}. (b) The CIE coordinates of the pc-LED are (0.3637, 0.3763) as shown by the red square. These CIE coordinates are similar to the CIE coordinates of the device made with $Cs_2NaInCl_6:Sb^{3+}$ (black circle).