Supplementary Information

Novel red-emitting $K_2Ca(PO_4)F:Eu^{2+}$ phosphor with a large Stokes shift

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EXPERIMENTAL SECTION

Chemicals and Materials. The starting materials were KF (Nacalai-Tesque, ≥99.00%), K_2CO_3 (Sigma-Aldrich, ≥99.995%), $CaHPO_4$ (Merck, ≥98.0%), $(NH_3)_2PO_4$ (Sigma-Aldrich, ≥99.00%), and Eu_2O_3 (Shin-Etsu, ≥99.9%). All of these chemicals were used without further purification. The phosphor samples were sintered in aluminum oxide crucibles.

Preparation. We prepared samples of $K_2CaPO_4F:Eu^{2+}$ (Eu = 0.01, FOLP:Eu^{2+}) by using a conventional high-temperature, solid-state reaction. The powder mixtures were then placed in aluminum oxide crucible and fired at 1223 K for 6 h in a reducing atmosphere of H_2/N_2 (5/95). The sintered samples were washed with distilled water. To obtain an X-ray diffraction pattern (XRD), a single crystal with a size of about 80 × 30 × 20 μm was picked from the sintered sample.

Characterization. XRD patterns of powdered FOLP:Eu^{2+} samples were measured on the BL02B1 beamline (wavelength 0.35450 Å) at the SPring-8 synchrotron radiation facility. The crystal structure was solved using direct methods with SIR2004.[1] The refinement of the structure was carried out by the method of least squares using SHELXL-97.[2] The solid-state nuclear magnetic resonance experiments were performed at 11.74 T on a JNM-ECZ500R (JEOL, Tokyo, Japan) equipped with a 3.2-mm cross-polarization magic angle spinning (CPMAS) probe at room temperature. The CPMAS spectra of ^{31}P at a frequency of 202.5 MHz and ^{19}F at a frequency of 470.6 MHz were obtained with a pulse length of 0.1 μs, a relaxation delay of 60 s, and a sample spinning frequency of 18 kHz.

Photoluminescence (PL) spectra under continuous excitation and photoluminescence excitation (PLE) spectra of the phosphor samples were measured at room temperature with a multichannel optical analyzers (PMA C5966-31, Hamamatsu Photonics, Shizuoka, Japan). The internal quantum efficiency value was determined from luminescence spectra obtained with a 407-nm laser-diode excitation of phosphor samples mounted in an integrating sphere.[3] For detection, we used a CAS 140B-152 spectrometer (Instrument Systems, Munich, Germany). Time-resolved luminescence spectra were measured with a pulsed, 355-nm laser with an excitation duration of 7 ns and a repetition rate of 10 Hz (LS-2134UTFFi, LOTIS TII, Minsk, Belarus). The monitoring wavelength was 650 nm.

Standard and constrained density functional theory calculations were performed using a projector-augmented wave method with a Perdew–Burke–Ernzerhof exchange-correlation functional implemented in VASP code.[4-7] A plane-wave cutoff energy of 500 eV was used to describe the wave functions for the unit cell containing 144 atoms ($K_{32}Ca_{15}EuP_{16}O_{64}F_{16}$), which is a 2 × 2 × 1 supercell of the primitive cell experimentally defined for a Eu-free system. Brillouin zone integration to

calculate the total energy was performed with a 2 × 2 × 1 Monkhorst–Pack k-mesh. The DFT + U method[8] with an effective U value (U_{eff}) of 7 eV for the Eu atom was used to account for the strong correlation of the 4f state. Typical values of U_{eff} reported that Eu^{2+} compounds are > 6 eV.[9,10] A CAS 140B-152 spectrometer was also used to obtain luminous flux, colour coordinates, and colour temperature from a pc-LED operated in an integrating sphere.

Fabrication of pc-LEDs. Phosphors of different emission colours were mixed at the following weight ratios to provide white emission of specified colour coordinates: FOLP:Eu^{2+}/$(Ca,Sr,Eu)_7(SiO_3)_6Cl_2$/$(Ca,Sr)_5(PO_4)_3Cl$:$Eu^{2+}$ = 6.5/2.0/1.5 for pc-LED1, and $(Sr,Ca)SiAlN_3$:Eu^{2+}/β-SiAlON:Eu^{2+}/$(Ca,Sr)_5(PO_4)_3Cl$:Eu^{2+} = 0.2/0.4/0.4 for pc-LED2. A phosphor paste was then made by dispersion of each of the above phosphor mixtures in translucent silicone resin at a concentration of 1.3 vol%. Finally, a pc-LED was fabricated by encapsulation of a near-ultraviolet chip (λ_p = 405 nm) on a white substrate with the phosphor paste, which was allowed to harden at 423 K for 90 min.

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Fig. S1 Configuration states of metal sites in FOLP:Eu^{2+} viewed along the *b*-axis. (a) Two Ca sites were coordinated by four O^{2-} ions and two F^{-} ions, (b) Four K sites were coordinated by eight O^{2-} ions and two F^{-} ions. (c) Two P sites were coordinated by four O^{2-} ions. Yellow spheres represent Ca^{2+} ions, red spheres represent O^{2-} ions, blue spheres represent F^{-} ions, purple spheres represent K^{+} ions, and grey spheres represent P^{5+} ions.

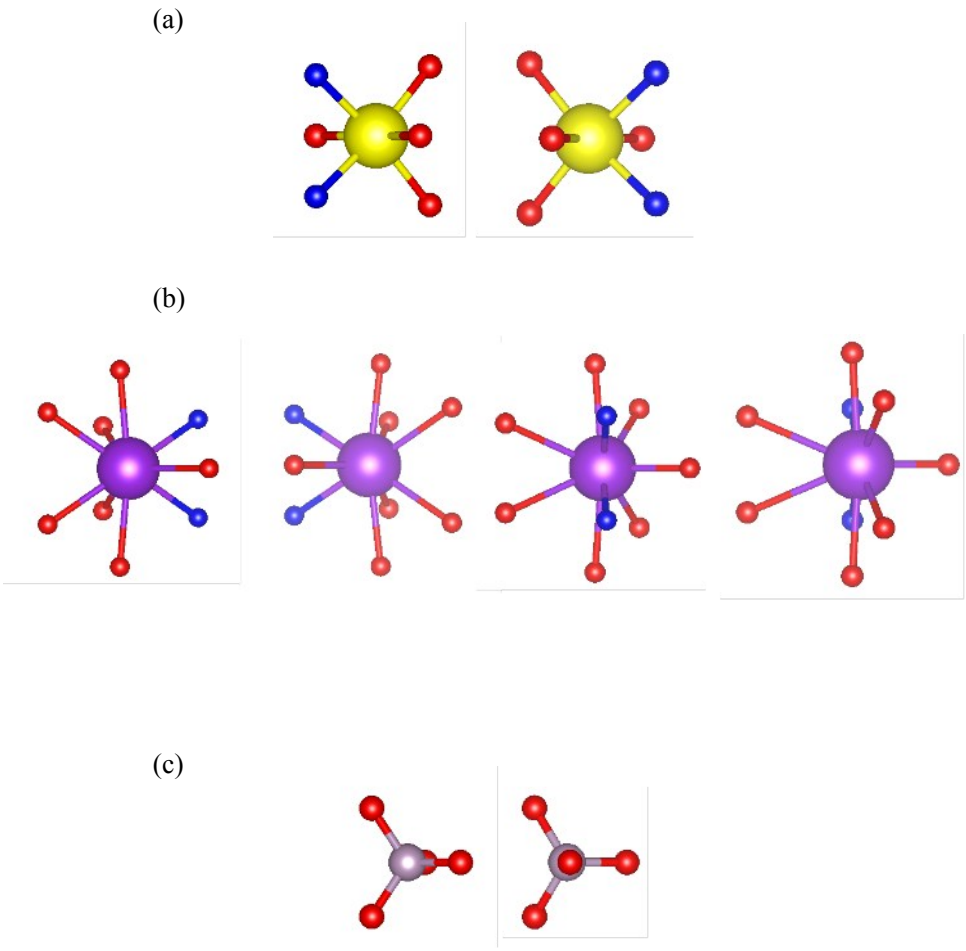

Fig. S2 Signal intensity of FOLP:Eu^{2+} as a function of contact time between 0.05 and 20 ms in $^{31}P\{^{19}F\}$-cross-polarization magic angle spinning. Because the signal intensity increased with contact time, F did not coordinate to P.

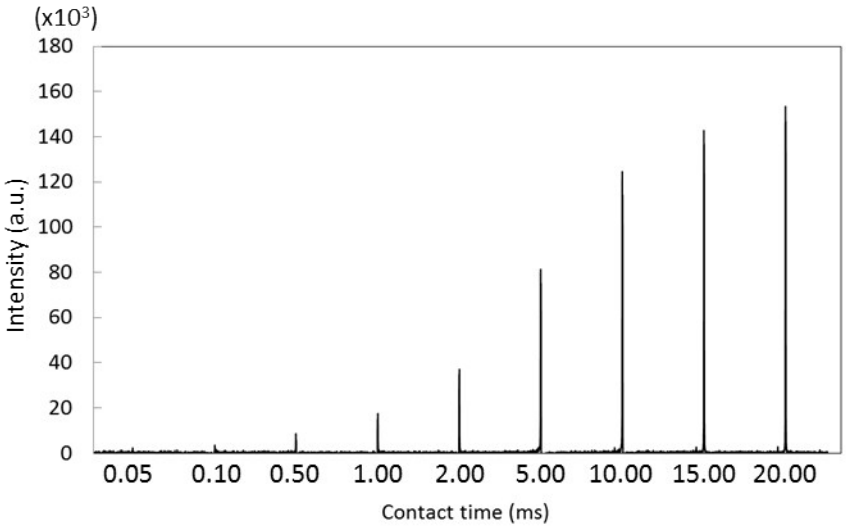

Fig. S3 Temperature dependence of lattice parameters of powdered FOLP:Eu^{2+} (Eu = 0.01). XRD patterns of powdered FOLP:Eu^{2+} sample were measured on the BL02B2 beamline (wavelength 0.4964 Å) at the SPring-8 synchrotron radiation facility. The lattice parameters were refined by Rietveld analysis using GSAS package.[11,12]

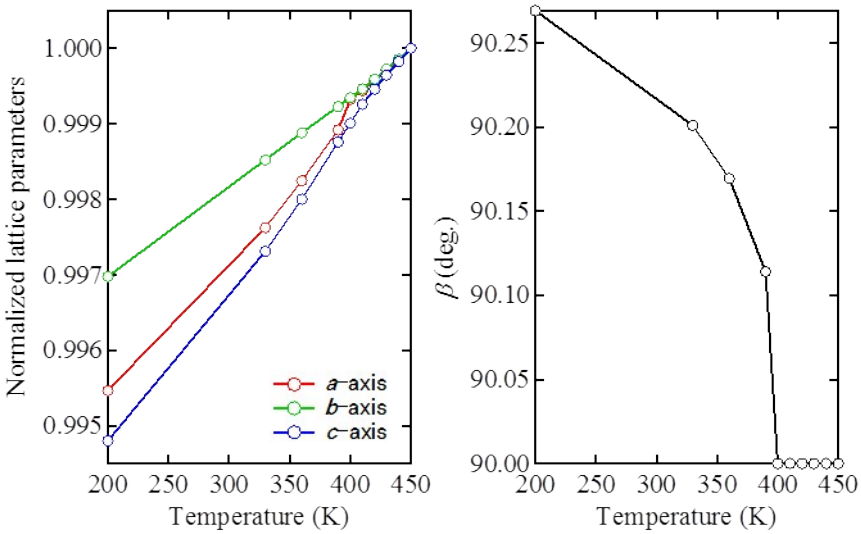

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Fig. S4 Dependence of PL spectra on the temperature of FOLP:Eu^{2+}.

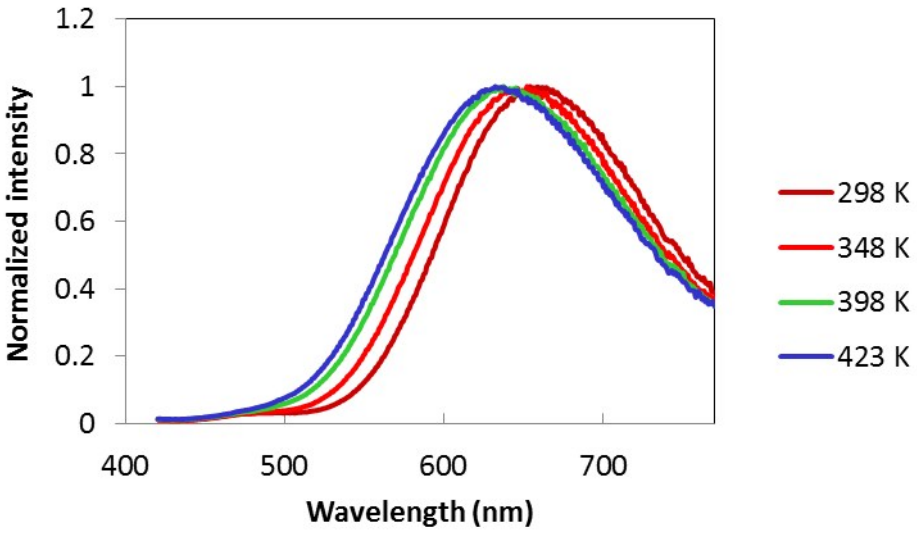
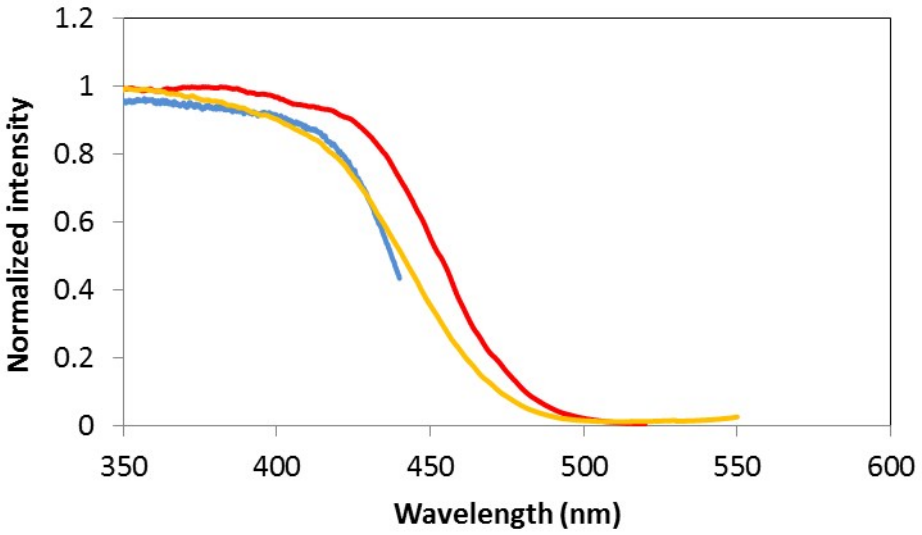


Fig. S5 Comparison of the PLE spectra of the phosphors. (a) PLE spectra of phosphors used in pc-LED1: $(Ca,Sr)_5(PO_4)_3Cl:Eu^{2+}$ (blue curve), $(Ca,Sr,Eu)_7(SiO_3)_6Cl_2$ (orange curve), and FOLP:Eu^{2+} (red curve). (b) PLE spectra of phosphors used in pc-LED2: $(Ca,Sr)_5(PO_4)_3Cl:Eu^{2+}$ (blue curve), β-SiAlON:Eu^{2+} (green curve), and (Sr,Ca) $AlSiN_3:Eu^{2+}$ (red curve).

(a)



(b)

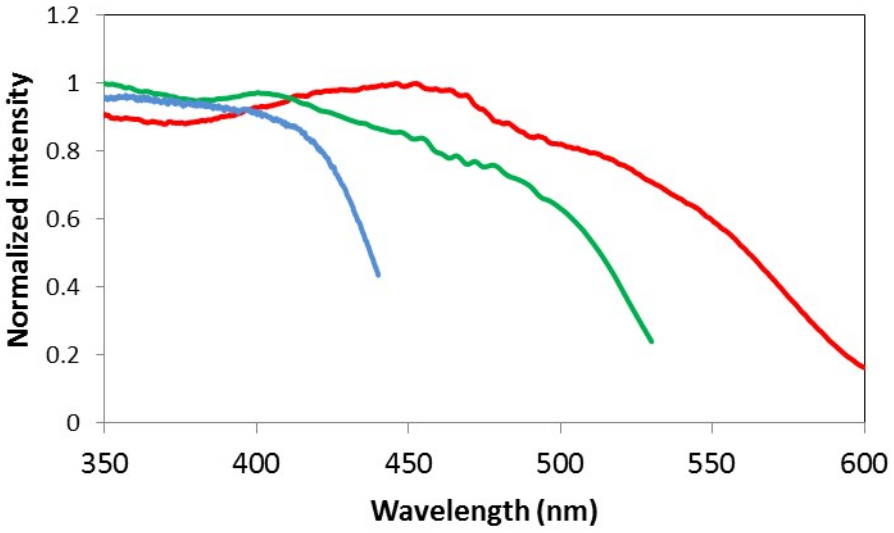


Table S1 Summary of crystallographic data for FOLP:Eu^{2+}.

Formula	$K_2Ca(PO_4)F:Eu^{2+}$ (Eu = 0.01)
Crystal system	Monoclinic
Space group	$P2_1/m$
Lattice parameters *a*	7.3161(4) Å
b	5.8560(6) Å
c	12.6434(1) Å
$\alpha = \gamma$	90 °
β	90.320 °
Cell volume	541.67(8) $Å^3$
Formula units per unit cell	4
Density	4.711 g/cm^3
R_factor_all	0.0209
R_factor_gt	0.0178
wR_factor_ref	0.0436
wR_factor_gt	0.0429
Goodness of fit	1.067
T	150 K
Radiation wavelength	λ = 0.35450 Å
Profile range	$0.80 \leq \theta \leq 20.76$
Total number of reflections	4775
Refine parameter	104

Table S2 Atomic coordinates and isotropic displacement parameters of FOLP:Eu^{2+} at 150 K.

Atom	x	y	z	Ueq / $Å^2$	Occupancy
Ca01	0.80199(3)	0.7500	0.076304(18)	0.00478(3)	0.99
Eu01	0.80199(3)	0.7500	0.076304(18)	0.00478(3)	0.01
Ca02	0.70720(3)	0.7500	0.565116(16)	0.00438(3)	0.99
Eu02	0.70720(3)	0.7500	0.565116(16)	0.00438(3)	0.01
K003	0.78425(3)	0.2500	0.41989(2)	0.00899(4)	1
K004	0.70332(4)	0.2500	0.93312(2)	0.00869(4)	1
K005	0.51539(3)	0.2500	0.68663(2)	0.00852(4)	1
K006	0.97756(4)	0.7500	0.81193(2)	0.01081(4)	1
P007	0.99058(4)	0.2500	0.66057(2)	0.00414(4)	1
P008	0.48832(4)	0.7500	0.83670(2)	0.00442(4)	1
F009	0.0000	0.5000	0.0000	0.00854(11)	1
F010	0.5000	0.0000	0.5000	0.00801(11)	1
O011	0.65718(13)	0.7500	0.90970(8)	0.01311(15)	1
O012	0.99976(11)	0.7500	0.21783(6)	0.00914(13)	1
O013	0.88731(9)	0.03479(12)	0.62419(5)	.01243(10)	1
O014	0.37493(11)	0.53512(14)	0.85990(6)	0.01780(14)	1
O015	0.54455(13)	0.7500	0.72003(7)	0.01079(13)	1
O016	0.81841(11)	0.7500	0.38966(7)	0.00886(12)	1

Table S3 Selected interatomic distances (Å) for FOLP:Eu^{2+} with standard deviations in parentheses.

Bond	Length	Bond	Length
Ca01 - O014	2.2639(7)	K005 - O016	2.6206(9)
Ca01 - F009	2.2778(2)	K005 - F010	2.7786(3)
Ca01 - O012	2.2949(8)	K005 - O014	2.9442(9)
Ca01 - O011	2.3526(10)	K005 - O015	2.9658(3)
Ca02 - O013	2.2504(7)	K005 - O013	3.1047(8)
Ca02 - F010	2.5947(19)	K006 - O011	2.6560(11)
Ca02 - O015	2.2975(9)	K006 - F009	2.7964(3)
Ca02 - O016	2.3672(9)	K006 - O012	2.9569(3)
K003 - F010	2.7418(3)	K006 - O013	2.9723(8)
K003 - O016	2.9636(3)	K006 - O014	3.2223(10)
K003 - O013	2.9677(8)	K006 - O015	3.3682(10)
K003 - O015	2.9780(10)	P007 - O016	1.5382(8)
K003 - O013	2.9801(8)	P007 - O012	1.5385(9)
K004 - F009	2.7476(3)	P007 - O013	1.5385(7)
K004 - O012	2.8997(9)	P007 - O013	1.5385(7)
K004 - O011	2.9620(3) .	P008 - O015	1.5336(9)
K004 - O014	2.9624(8)	P008 - O014	1.5363(7)
K004 - O014	3.0647(10)	P008 - O014	1.5364(7)
K004 - O011	3.3112(11)	P008 - O011	1.5380(9)

Table S4 Selected bond angles (°) for FOLP:Eu^{2+} with standard deviations in parentheses.

O014 - Ca01 - O014	95.04(5)	Ca02 - F010 - Ca02	180.000(10)
O014 - Ca01 - F009	172.37(2)	Ca02 - F010 - K003	91.613(9)
O014 - Ca01 - F009	92.47(2)	Ca02 - F010 - K005	90.461(8)
F009 - Ca01 - F009	79.992(10)	K003 - F010 - K005	89.704(9)
O014 - Ca01 - O012	94.67(3)	K005 - F010 - K005	180.000(12)
F009 - Ca01 - O012	86.017(17)	P008 - O011 - Ca01	153.32(6)
O014 - Ca01 - O011	93.64(3)	P008 - O011 - K006	115.39(5)
F009 - Ca01 - O011	84.55(2)	Ca01 - O011 - K006	91.29(3)
O012 - Ca01 - O011	167.68(3)	P008 - O011 - K004	98.668(18)
O013 - Ca02 - O013	95.65(4)	Ca01 - O011 - K004	81.951(18)
O013 - Ca02 - F010	172.53(2)	K006 - O011 - K004	86.91(2)
O013 - Ca02 - F010	91.79(2)	K004 - O011 - K004	162.61(4)
F010 - Ca02 - F010	80.773(9)	P008 - O011 - K004	73.76(4)
O013 - Ca02 - O015	91.27(2)	K006 - O011 - K004	162.61(4)
F010 - Ca02 - O015	87.76(2)	P008 - O011 - K004	73.76(4)
O013 - Ca02 - O016	96.16(2)	K006 - O011 - K004	170.85(4)
F010 - Ca02 - O016	83.796(17)	K004 - O011 - K004	91.76(2)
O015 - Ca02 - O016	168.91(3)	P007 - O013 - Ca02	172.73(5)
O016 - P007 - O012	112.07(5)	P007 - O013 - K003	91.97(3)
O016 - P007 - O013	108.80(3)	Ca02 - O013 - K003	83.13(2)
O012 - P007 - O013	108.57(3)	P007 - O013 - K006	96.56(3)
O013 - P007 - O013	110.00(6)	Ca02 - O013 - K006	88.64(2)
O015 - P008 - O014	109.37(4)	K003 - O013 - K006	170.97(3)
O014 - P008 - O014	109.98(7)	P007 - O013 - K003	96.84(3)
O015 - P008 - O011	111.00(5)	Ca02 - O013 - K003	89.68(2)
O014 - P008 - O011	108.56(4)	K003 - O013 - K003	106.03(2)
Ca01 - F009 - Ca01	180.000	K006 - O013 - K003	70.096(19)
Ca01 - F009 - K004	91.742(8)	P007 - O013 - K005	91.21(3)
K004 - F009 - K004	180.000(10)	Ca02 - O013 - K005	82.70(2)
Ca01 - F009 - K006	90.619(9)	K006 - O013 - K005	102.46(2)
K004 - F009 - K006	88.552(9)	K003 - O013 - K005	169.56(3)

Table S5 Crystallographic data for orthorhombic FOLP:Eu^{2+}.

Temp.		450K
Crystal system		Orthorhombic
Space group		*Pcmn*
Lattice parameters	*a*	7.3597(3) Å
	b	5.8880(13) Å
	c	12.742(3) Å

Table S6 Atomic coordinates and isotropic displacement parameters of orthorhombic FOLP:Eu^{2+} at 450 K.

	x	y	z	Ueq / $Å^2$	Occupancy
Ca01	0.70244(2)	0.2500	0.571595(15)	0.01174(4)	0.9944(5)
Eu01	0.70244(2)	0.2500	0.571595(15)	0.01174(4)	0.0056(5)
K002	0.79169(4)	-0.2500	0.42587(3)	0.02607(6)	1
K003	0.49394(5)	-0.2500	0.68681(2)	0.02771(6)	1
P004	0.98791(3)	-0.2500	0.661341(19)	0.01027(4)	1
F005	0.5000	0.5000	0.5000	0.02035(13)	1
O006	0.52497(16)	0.2500	0.72045(7)	0.02731(19)	1
O007	0.83467(14)	0.2500	0.40188(9)	0.0281(2)	1
O008	0.87943(12)	0.53611(14)	0.63300(6)	0.03291(17)	1

Table S7 Calculated absorption, emission and Stokes shift of FOLP:Eu^{2+} comparted with the experimental data.

	Calc.	Exp.
E_{tot} (A_0)	-892.50722 eV	—
E_{tot} (A_0*)	-888.25072 eV	—
E_{tot} (A*)	-888.97984 eV	—
E_{tot} (A)	-891.85859 eV	—
E_{abs}	4.26 eV (291 nm)	3.26 eV (380 nm)
E_{em}	2.88 eV (431 nm)	1.88 eV (658 nm)
ΔS	1.38 eV	1.38 eV

Table S8 Performance of the fabricated pc-LEDs.

Pc-LED1: a nUV chip (λp = 405 nm) coupled with a mixture of FOLP:Eu^{2+}, the yellow phosphor $(Ca,Sr,Eu)_7(SiO_3)_6Cl_2$ and the blue phosphor $(Ca,Sr)_5(PO_4)_3Cl:Eu^{2+}$. Pc-LED2: a nUV chip coupled with a mixture of the red phosphor $(Sr,Ca)AlSiN_3:Eu^{2+}$, the green phosphor β-SiAlON:Eu^{2+} and $(Ca,Sr)_5(PO_4)_3Cl:Eu^{2+}$. The performance of the pc-LEDs was observed at an operational current of 350 mA.

Pc-LED	Luminous flux (lm)	Colour rendering index (Ra)	Colour temperature (K)
Pc-LED1	63	89	3970
Pc-LED2	60	87	3900