# Electronic Supplementary Information (ESI)

# Structural Evolution of Organic-inorganic hybrid crystals for high colour-rendering white LEDs

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**Experimental section**

**(1) Materials and preparation**

All reagent materials used in this work, including hydrofluoric acid (HF, 39 wt. %), tetraethylammonium fluoride tetrahydrate ($[N(CH_3)_4]_2F\cdot4H_2O$), germanium oxide ($GeO_2$), hexafluorosilicic acid solution ($H_2SiF_6$, 30 wt. %), hexafluorotitanic acid solution ($H_2TiF_6$, 50 wt. %), potassium permanganate ($KMnO_4$) and hydrogen peroxide ($H_2O_2$, 30 wt. %) were of analytical grade without any further purification. YAG:$Ce^{3+}$ ceramic chip was purchased from Shenzhen looking long technology co., LTD.

$[N(CH_3)_4]_2XF_6:Mn^{4+}$ (X=Si, Ge, and Ti) crystals were grown by the solvent evaporation method. Firstly, 10 mmol $XO_2$ (X=Si, Ge, and Ti) were put into a plastic beaker containing 10 mL of magnetically stirred 39 % HF solution until completely dissolved. Then, 0.05 mmol $K_2MnF_6$ and 50 mmol $[N(CH_3)_4]_2F\cdot4H_2O$ were added into the colorless transparent solution sequentially and stirred continuously at room temperature for 1 hour. The transparent solution was put into the fume hood. After one week, red-emitting $[N(CH_3)_4]_2XF_6:Mn^{4+}$ crystals grew up from this solution.

**(2) Fabrication of devices**

The single red LEDs was fabricated by coating the crystals on the GaN chips with a little silica gel. The white LEDs are obtained by coating the YAG:$Ce^{3+}$ ceramic chips on the red LEDs with a little silica gel.

**(3) Characterization**

Single-crystal X-ray diffraction of $[N(CH_3)_4]_2XF_6:Mn^{4+}$ crystals were selected

and on a SuperNova, AtlasS2 diffractometer (Rigaku Oxford Diffraction). Data was collected with Cu Kα or Mo Kα radiation at 150 K and 293 K, respectively. Using Olex2,[1] the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation. All non-hydrogen atoms were located in different Fourier syntheses and finally refined with anisotropic displacement parameters. All hydrogen atoms of the organic ligands were placed by geometrical considerations and isotropically refined with fixed U values using a riding model. The fourier transform infrared spectra (FT-IR) were measured on a fourier transform infrared spectrograph (FT-IR, NICOLET-IS10, Thermo Nicolet Corporation). The surface element composition of $[N(CH_3)_4]_2XF_6:Mn^{4+}$ was observed by an attached energy dispersive X-ray spectrometer (EDS). Thermogravimetry (TG) curves were measured on a Mettler TGA/DSC3+ thermal analyzer at a heating rate 10°C/min under $N_2$. The photo-luminescent spectra at room- and high-temperature were measured by a Cary Eclipse FL1011M003 (Varian) spectrofluorometer. The emission spectra, quantum efficiency (QE), and decay curves were collected on an F-7000 (Hitachi) spectrofluorometer. The optical performance of the LED devices was recorded on a high accurate array spectrometer (HSP6000).

**Figures**

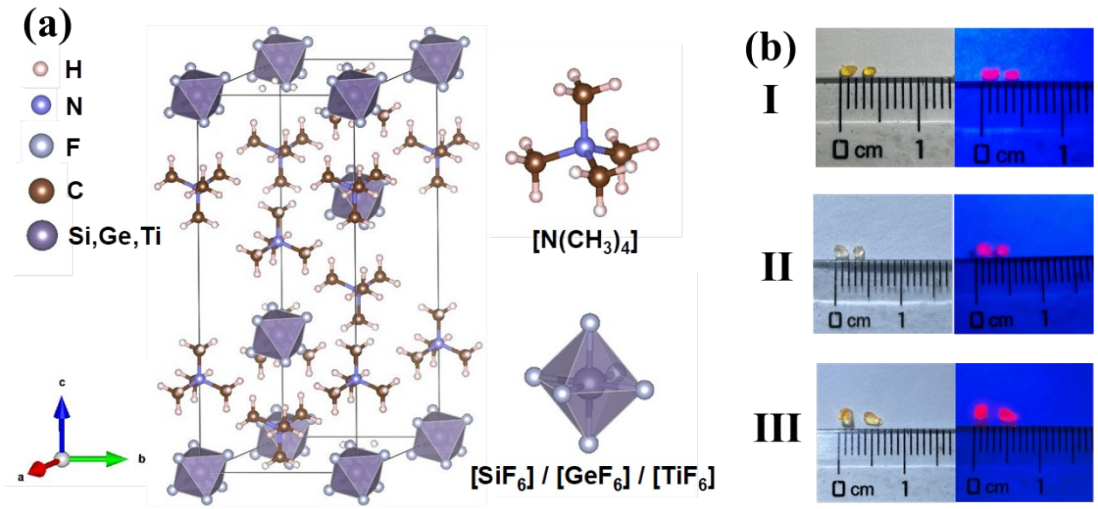


**Figure S1** Crystal structure of $[N(CH_3)_4]_2XF_6:Mn^{4+}$ at 150 K, (b) photographs of $[N(CH_3)_4]_2XF_6:Mn^{4+}$ irradiated by the natural and blue light (I: $[N(CH_3)_4]_2SiF_6:Mn^{4+}$, II: $[N(CH_3)_4]_2GeF_6:Mn^{4+}$, and III: $[N(CH_3)_4]_2TiF_6:Mn^{4+}$).

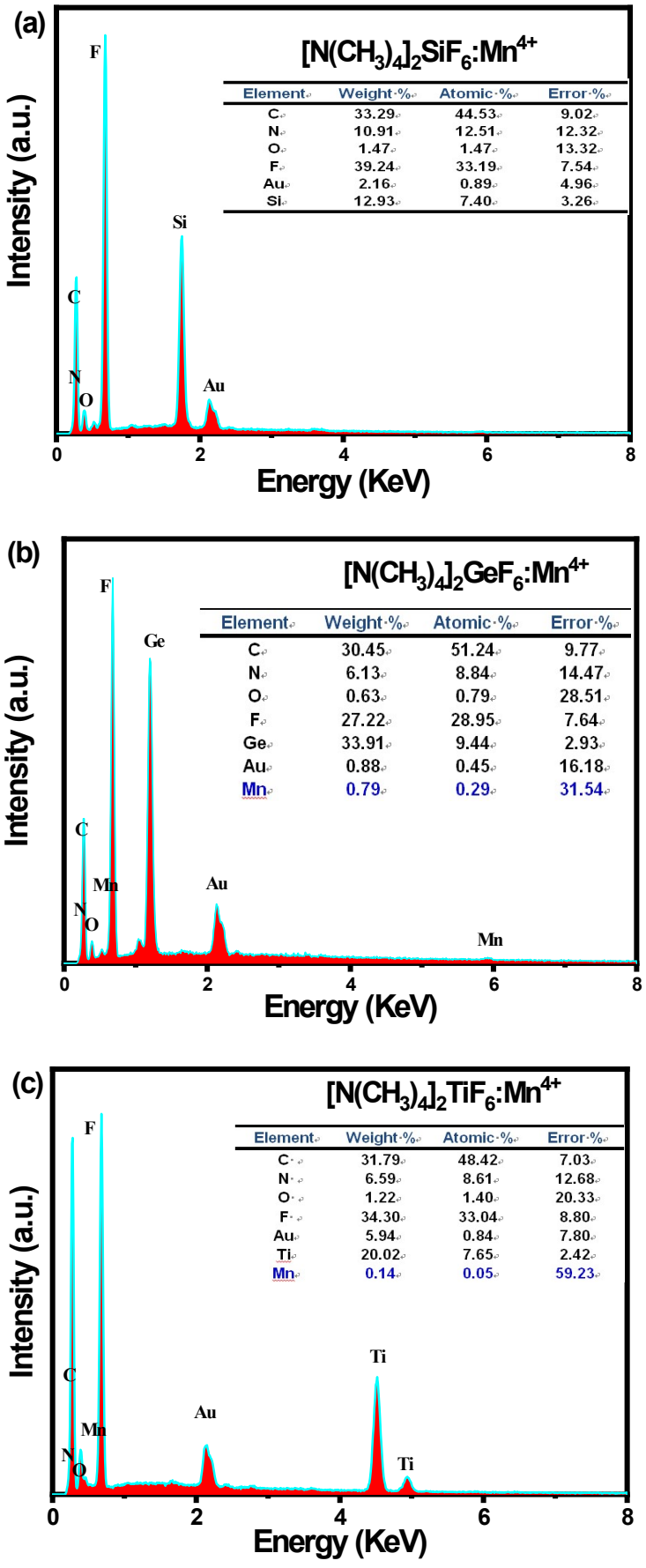


**Figure S2** EDS spectra of $[N(CH_3)_4]_2XF_6:Mn^{4+}$

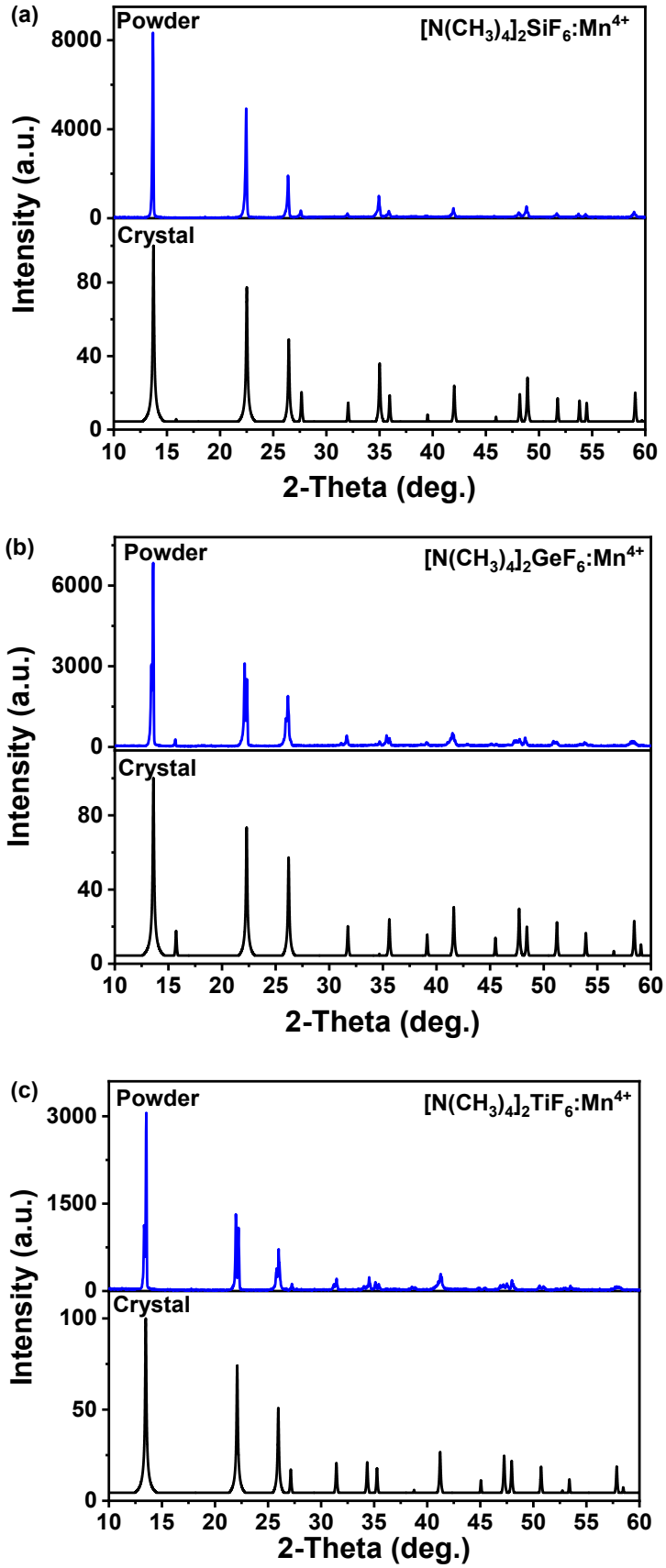


**Figure S3** XRD patterns of $[N(CH_3)_4]_2XF_6:Mn^{4+}$ powders and crystals at 293 K.

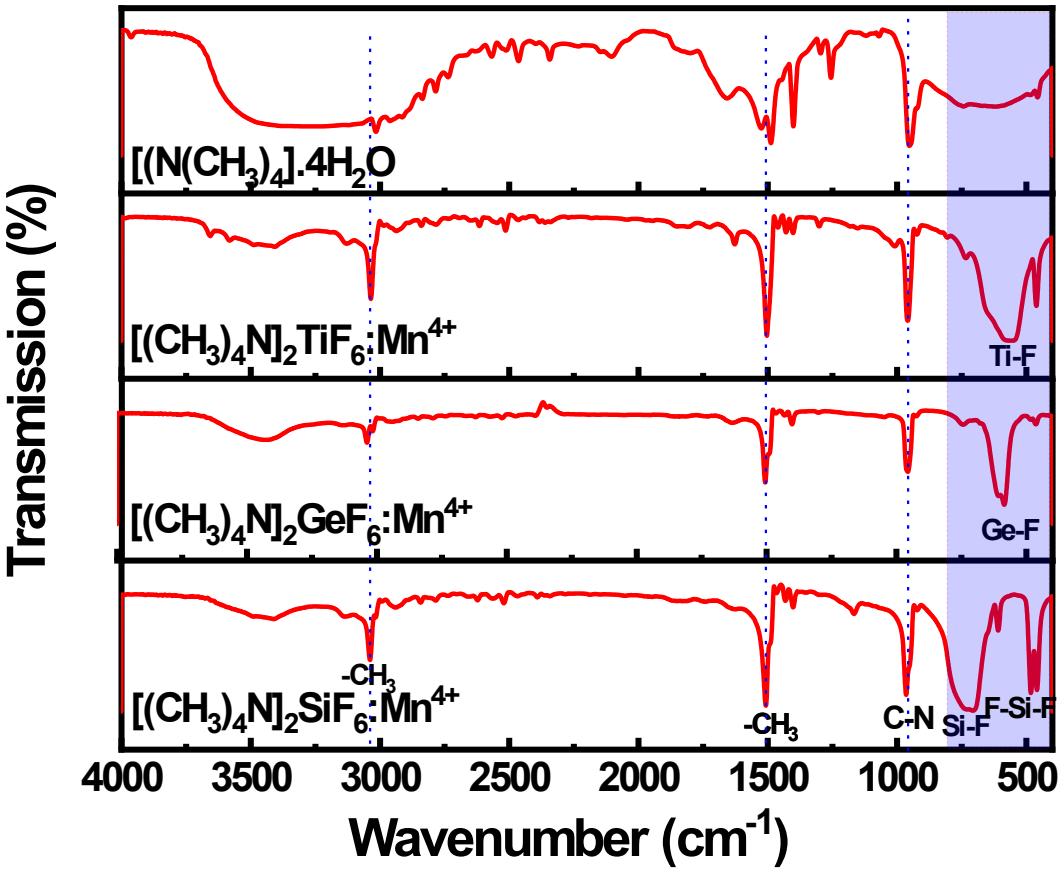


**Figure S4** IR spectra of $[N(CH_3)_4]_2 \cdot 4H_2O$ and $[N(CH_3)_4]_2XF_6:Mn^{4+}$.

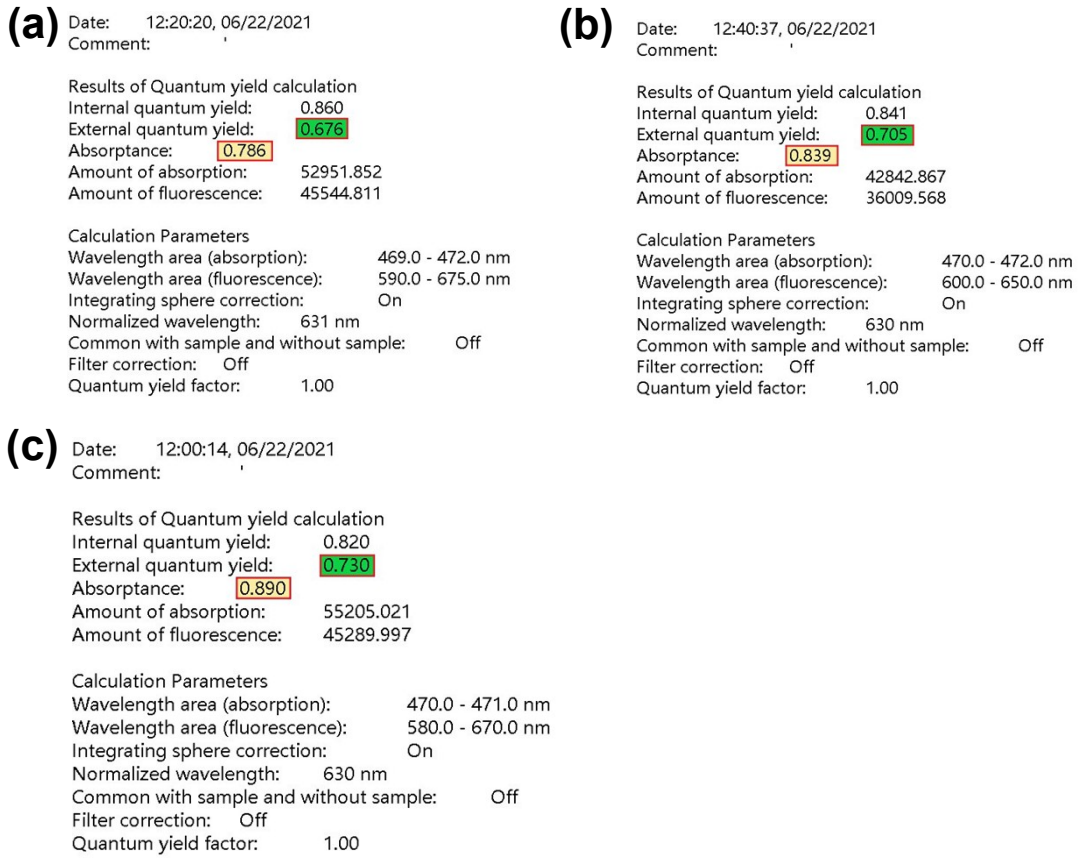


**Figure S5** Quantum efficiency of (a) $[N(CH_3)_4]_2SiF_6:Mn^{4+}$, (b) $[N(CH_3)_4]_2GeF_6:Mn^{4+}$, and (c) $[N(CH_3)_4]_2TiF_6:Mn^{4+}$ single crystals.

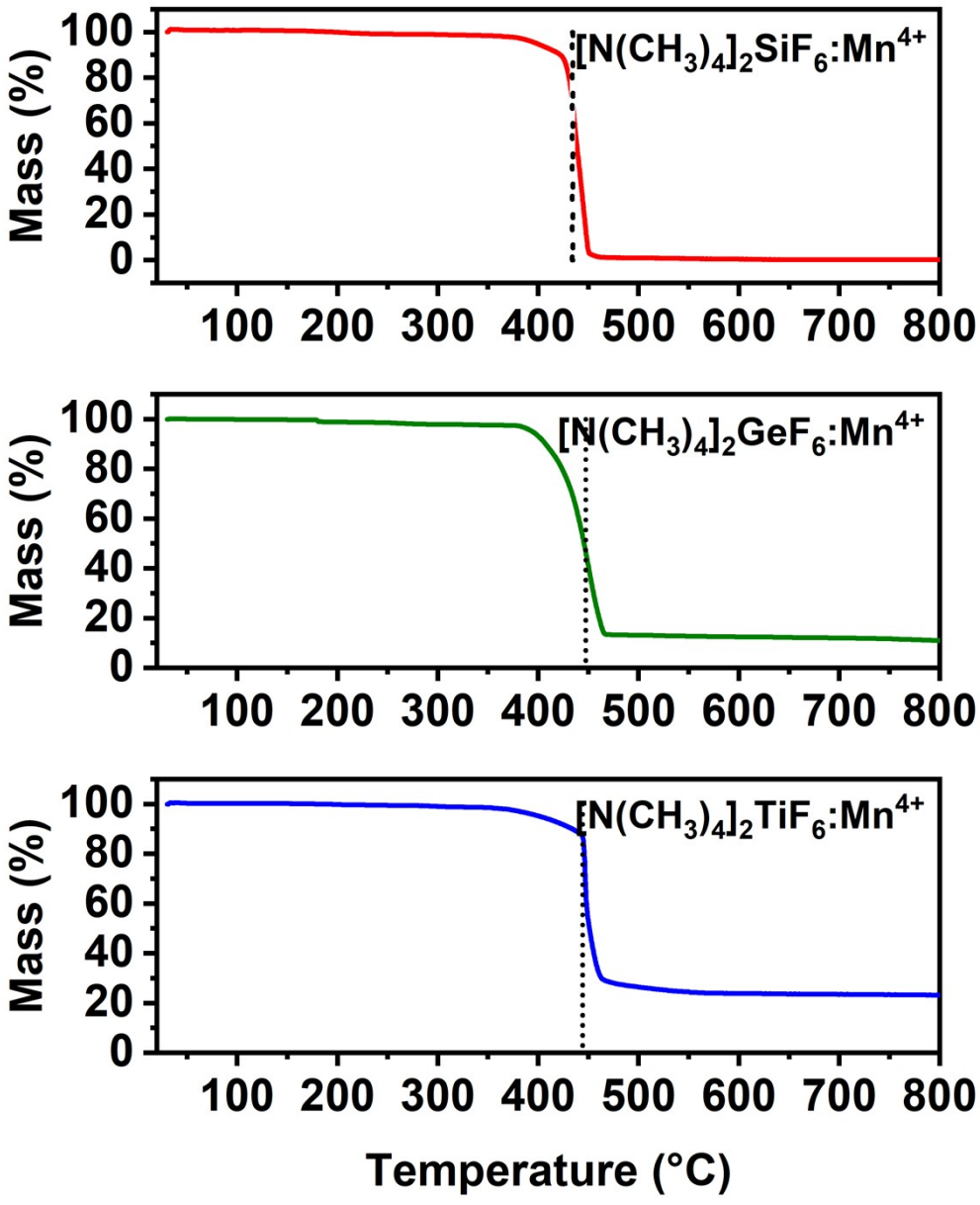


**Figure S6**. TG curves of $[N(CH_3)_4]_2XF_6:Mn^{4+}$ single-crystals

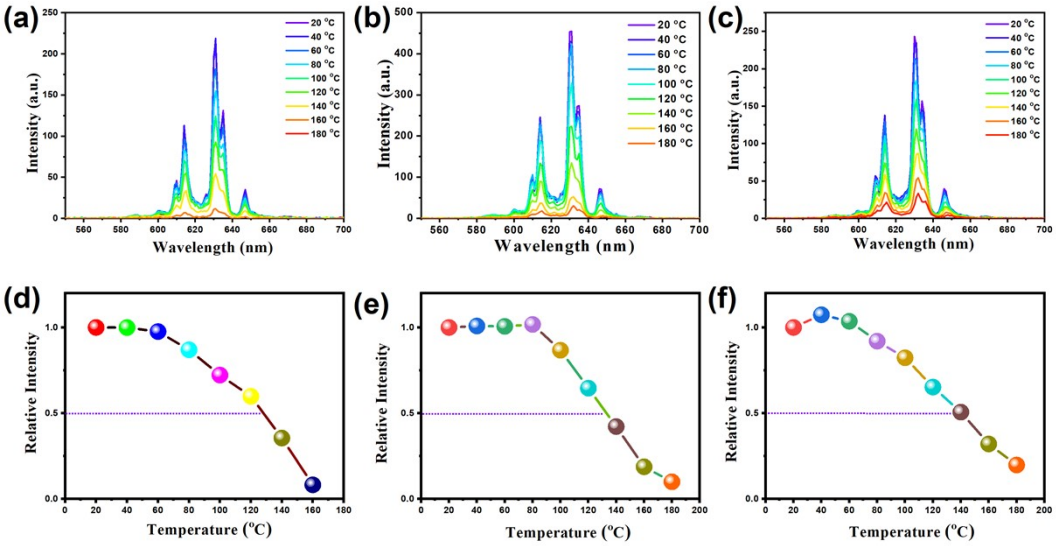


**Figure S7** (a, b, c) Emission spectra of $[N(CH_3)_4]_2SiF_6:Mn^{4+}$, $[N(CH_3)_4]_2GeF_6:Mn^{4+}$, and $[N(CH_3)_4]_2TiF_6:Mn^{4+}$ at different temperatures, (d, e, f) and dependence of the emission intensity on the temperature.

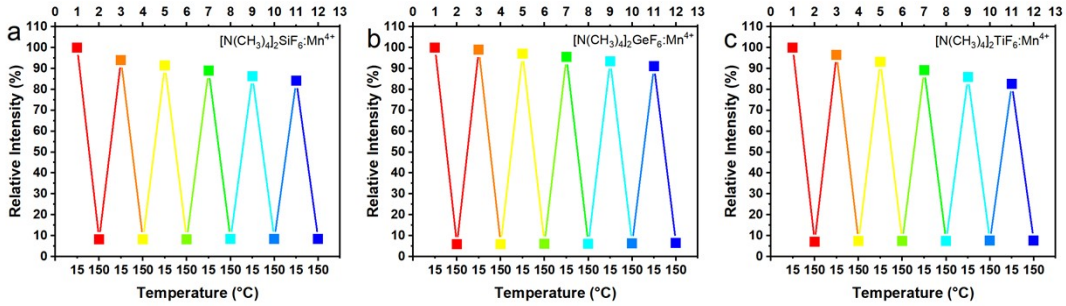


**Figure S8** (a, b, c) PL relative intensities of $[N(CH_3)_4]_2SiF_6:Mn^{4+}$, $[N(CH_3)_4]_2GeF_6:Mn^{4+}$, and $[N(CH_3)_4]_2TiF_6:Mn^{4+}$ single-crystals at 25 °C and 150 °C during five heating-cooling cycles.

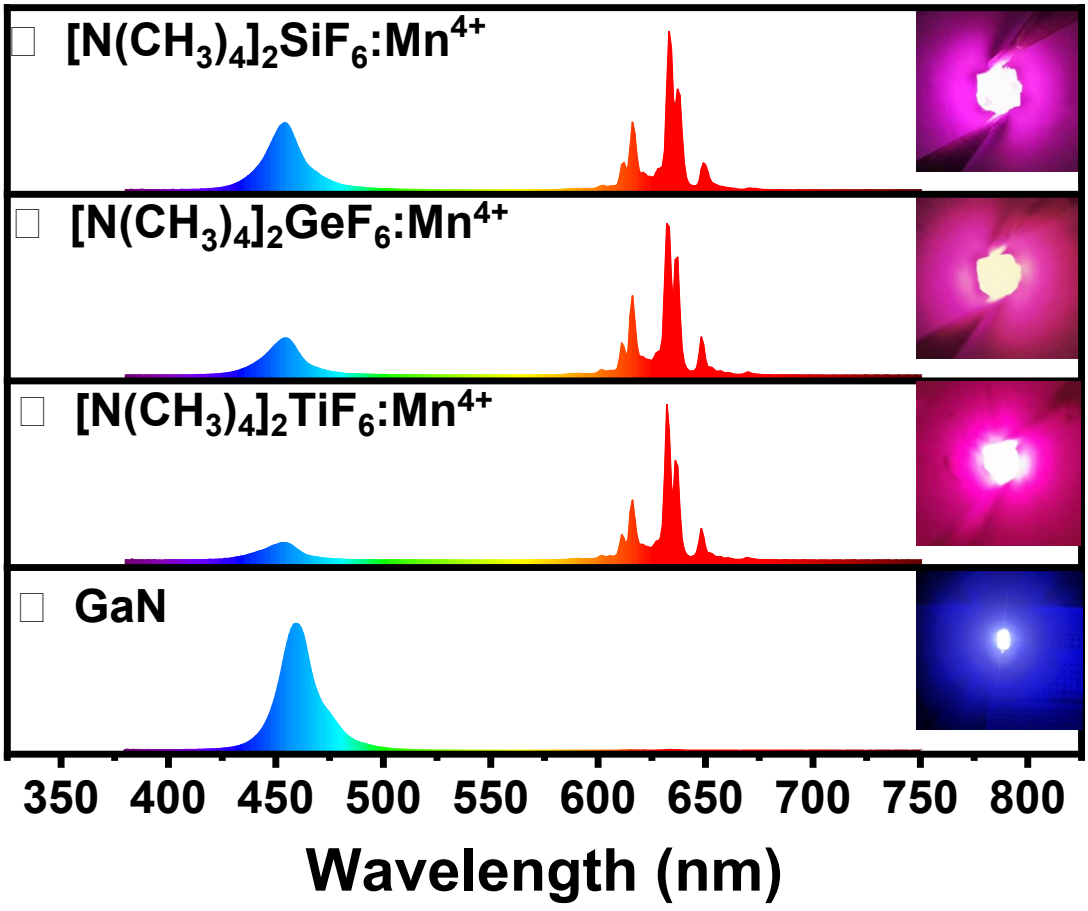


**Figure S9** The spectrum of single red LED chip coated by merging $[N(CH_3)_4]_2XF_6:Mn^{4+}$ single-crystals and epoxy resin on blue GaN chips (~460 nm) at 20 mA current.

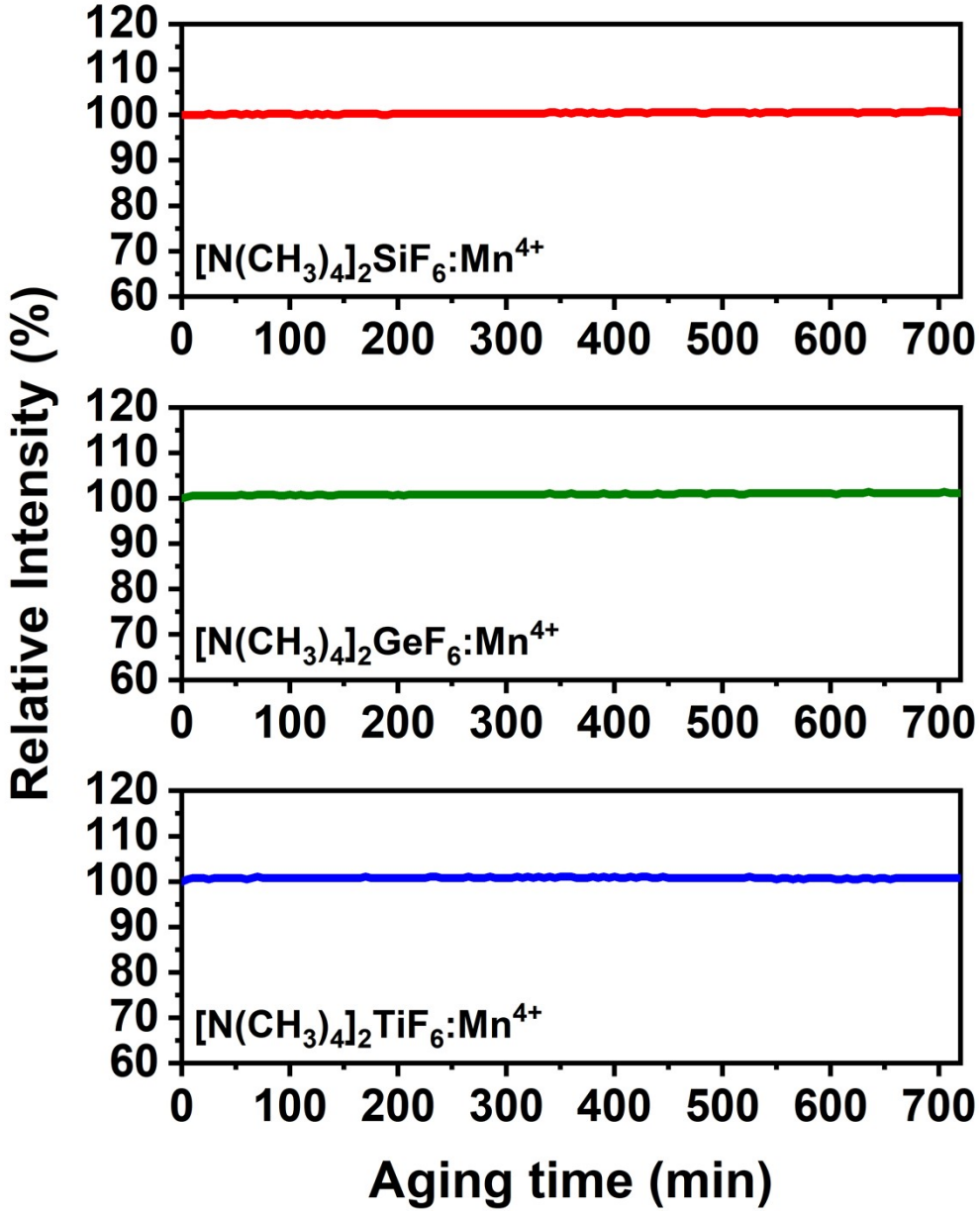


**Figure S10** Relative luminous flux curves of single red LEDs coated by merging $[N(CH_3)_4]_2XF_6:Mn^{4+}$ (X=Si, Ge, and Ti) single-crystals under a current of 20 mA with aging time of 720 min.

**Tables**

**Table S1** Crystal data and structure refinement for $[N(CH_3)_4]_2SiF_6:Mn^{4+}$ at 150 K ($NMe_4SiF_6$ 150K).

| Identification code | $NMe_4SiF_6$ 150K |
|---|---|
| Empirical formula | $C_8H_{24}F_6N_2Si$ |
| Formula weight | 290.37 |
| Temperature/K | 150.00(10) |
| Crystal system | trigonal |
| Space group | $R\bar{3}$ |
| $a$/Å | 7.7802(8) |
| $b$/Å | 7.7802(8) |
| $c$/Å | 19.544(2) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 120 |
| $V$/Å$^3$ | 1024.5(2) |
| $Z$ | 3 |
| $\rho_{calc}$g/cm$^3$ | 1.412 |
| $\mu$/mm$^{-1}$ | 2.061 |
| F(000) | 462.0 |
| Crystal size/mm$^3$ | 0.08 × 0.04 × 0.03 |

| | |
|---|---|
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 13.592 to 143.986 |
| Index ranges | $-8 \leq h \leq 7$, $-7 \leq k \leq 9$, $-23 \leq l \leq 18$ |
| Reflections collected | 714 |
| Independent reflections | 434 [$R_{int}$ = 0.0423, $R_{sigma}$ = 0.0415] |
| Data/restraints/parameters | 434/0/30 |
| Goodness-of-fit on $F^2$ | 1.095 |
| Final *R* indexes [I>=2σ (I)] | $R_1$ = 0.0714, $wR_2$ = 0.1828 |
| Final *R* indexes [all data] | $R_1$ = 0.0716, $wR_2$ = 0.1829 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.77/-0.50 |

**Table S2** Bond lengths [Å] for $[N(CH_3)_4]_2SiF_6$:$Mn^{4+}$ at 150 K ($NMe_4SiF_6$ 150K).

| | |
|---|---|
| C1—N1 | 1.498(3) |
| C2—N1 | 1.502(6) |
| N1—C1$^1$ | 1.498(3) |
| N1—C1$^2$ | 1.498(3) |
| F1—Si1 | 1.693(2) |
| Si1—F1$^3$ | 1.693(2) |
| Si1—F1$^4$ | 1.693(2) |

| | |
|---|---|
| Si1—F1[5] | 1.693(2) |
| Si1—F1[6] | 1.693(2) |
| Si1—F1[7] | 1.693(2) |

[1]1-Y,1+X-Y,+Z; [2]+Y-X,1-X,+Z; [3]2-Y,1+X-Y,+Z; [4]1+Y-X,2-X,+Z; [5]1-Y+X,+X,1-Z; [6]2-X,2-Y,1-Z; [7]+Y,1-X+Y,1-Z

**Table S3** Bond Angles[˚] for $[N(CH_3)_4]_2SiF_6:Mn^{4+}$ at 150 K ($NMe_4SiF_6$ 150K).

| **Bond** | **Angle/ ˚** | **Bond** | **Angle/ ˚** |
|---|---|---|---|
| C1[1]—N1—C1[2] | 109.70(17) | F1[5]—Si1—F1[4] | 180.0 |
| C1—N1—C1[1] | 109.70(17) | F1[6]—Si1—F1[5] | 89.90(9) |
| C1—N1—C1[2] | 109.70(17) | F1[3]—Si1—F1[7] | 90.10(9) |
| C1—N1—C2 | 109.25(17) | F1[6]—Si1—F1[7] | 89.90(9) |
| C1[2]—N1—C2 | 109.25(17) | F1[3]—Si1—F1[6] | 180.0 |
| C1[1]—N1—C2 | 109.25(17) | F1[7]—Si1—F1[4] | 89.90(9) |

| | | | |
|---|---|---|---|
| F1—Si1—F1[3] | 89.90(9) | F1—Si1—F1[5] | 89.90(9) |
| F1[3]—Si1—F1[4] | 89.90(9) | F1—Si1—F1[7] | 180.0 |
| F1[3]—Si1—F1[5] | 90.10(9) | F1—Si1—F1[6] | 90.10(9) |
| F1—Si1—F1[4] | 90.10(9) | F1[7]—Si1—F1[5] | 90.10(9) |
| F1[6]—Si1—F1[4] | 90.10(9) | | |

[1]1-Y,1+X-Y,+Z; [2]+Y-X,1-X,+Z; [3]+Y,1-X+Y,1-Z; [4]1+Y-X,2-X,+Z; [5]1-Y+X,+X,1-Z; [6]2-Y,1+X-Y,+Z; [7]2-X,2-Y,1-Z

**Table S4** Crystal data and structure refinement for $[N(CH_3)_4]_2SiF_6:Mn^{4+}$ at 293 K ($NMe_4SiF_6$ 293K).

| Identification code | $NMe_4SiF_6$ 293K |
|---|---|
| Empirical formula | $C_8H_{24}F_6N_2Si$ |
| Formula weight | 290.38 |
| Temperature/K | 293.00(10) |
| Crystal system | tetragonal |
| Space group | *I*4/*m* |

| | |
|---|---|
| *a*/Å | 7.8924(10) |
| *b*/Å | 7.8924(10) |
| *c*/Å | 11.163(4) |
| *α*/° | 90 |
| *β*/° | 90 |
| *γ*/° | 90 |
| Volume/Å$^3$ | 695.3(3) |
| *Z* | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.387 |
| μ/mm$^{-1}$ | 0.220 |
| F(000) | 308.0 |
| Crystal size/mm$^3$ | 0.3 × 0.25 × 0.15 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.322 to 60.584 |
| Index ranges | -10 ≤ h ≤ 10, -7 ≤ k ≤ 10, -15 ≤ l ≤ 15 |
| Reflections collected | 493 |
| Independent reflections | 493 [$R_{int}$ = ?, $R_{sigma}$ = 0.0692] |
| Data/restraints/parameters | 493/0/27 |
| Goodness-of-fit on $F^2$ | 1.143 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0543, $wR_2$ = 0.1135 |
| Final R indexes [all data] | $R_1$ = 0.0583, $wR_2$ = 0.1185 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.26/-0.23 |

**Table S5** Bond lengths [Å] for $[N(CH_3)_4]_2SiF_6:Mn^{4+}$ at 293 K ($NMe_4SiF_6$ 293K).

| | |
|---|---|
| Si1—F1[1] | 1.677(2) |
| Si1—F1[2] | 1.677(2) |
| Si1—F1 | 1.677(2) |
| Si1—F1[3] | 1.677(2) |
| Si1—F2[1] | 1.676(4) |
| Si1—F2 | 1.676(4) |
| N1—C1[4] | 1.491(2) |
| N1—C1 | 1.491(2) |
| N1—C1[5] | 1.491(2) |
| N1—C1[6] | 1.491(2) |

[1]-X,-Y,1-Z; [2]-Y,+X,+Z; [3]+Y,-X,1-Z; [4]1/2-Y,1/2+X,1/2-Z; [5]-1/2+Y,1/2-X,1/2-Z; [6]-X,1-Y,+Z

**Table S6** Bond Angles[˚] for $[N(CH_3)_4]_2SiF_6:Mn^{4+}$ at 293 K ($NMe_4SiF_6$ 293K).

| **Bond** | **Angle/ ˚** | **Bond** | **Angle/ ˚** |
|---|---|---|---|
| $F1^1$—Si1—$F1^2$ | 90.0 | F2—Si1—$F1^2$ | 90.0 |
| $F1^1$—Si1—F1 | 180.0 | $F2^1$—Si1—$F1^3$ | 90.0 |
| $F1^1$—Si1—$F1^3$ | 90.0 | F2—Si1—$F1^1$ | 90.0 |
| $F1^3$—Si1—F1 | 90.0 | $F2^1$—Si1—F2 | 180.0 |
| $F1^2$—Si1—F1 | 90.0 | $C1^4$—N1—$C1^5$ | 109.53(12) |
| $F1^2$—Si1—$F1^3$ | 180.0 | C1—N1—$C1^6$ | 109.53(12) |
| $F2^1$—Si1—F1 | 90.0 | C1—N1—$C1^5$ | 109.4(2) |
| $F2^1$—Si1—$F1^2$ | 90.0 | C1—N1—$C1^4$ | 109.53(12) |
| F2—Si1—$F1^3$ | 90.0 | $C1^6$—N1—$C1^4$ | 109.4(2) |
| F2—Si1—F1 | 90.0 | $C1^6$—N1—$C1^5$ | 109.53(12) |

| | |
|---|---|
| $F2^{1}$—Si1—$F1^{1}$ | 90.000 |

[1]-X,-Y,1-Z; [2]+Y,-X,1-Z; [3]-Y,+X,+Z; [4]1/2-Y,1/2+X,1/2-Z; [5]-X,1-Y,+Z; [6]-1/2+Y,1/2-X,1/2-Z

**Table S7** Crystal data and structure refinement for $[N(CH_3)_4]_2GeF_6:Mn^{4+}$ at 150 K ($NMe_4GeF_6$ 150K).

| Identification code | $NMe_4GeF_6$ 150K |
|---|---|
| Empirical formula | $C_8H_{24}F_6N_2Ge$ |
| Formula weight | 334.87 |
| Temperature/K | 150.00(10) |
| Crystal system | trigonal |
| Space group | $R\bar{3}$ |
| *a*/Å | 7.8554(5) |
| *b*/Å | 7.8554(5) |
| *c*/Å | 19.6666(17) |
| *α*/° | 90 |

| | |
|---|---|
| $\beta$/° | 90 |
| $\gamma$/° | 120 |
| $V$/Å$^3$ | 1050.98(16) |
| $Z$ | 3 |
| $\rho_{calc}$ g/cm$^3$ | 1.587 |
| $\mu$/mm$^{-1}$ | 2.237 |
| F(000) | 516.0 |
| Crystal size/mm$^3$ | 0.3 × 0.25 × 0.2 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 7.284 to 73.432 |
| Index ranges | -12 ≤ h ≤ 13, -13 ≤ k ≤ 12, -32 ≤ l ≤ 32 |
| Reflections collected | 3570 |
| Independent reflections | 1112 [$R_{int}$ = 0.0747, $R_{sigma}$ = 0.0577] |
| Data/restraints/parameters | 1112/0/29 |
| Goodness-of-fit on F$^2$ | 1.149 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0668, w$R_2$ = 0.1734 |
| Final R indexes [all data] | $R_1$ = 0.0671, w$R_2$ = 0.1740 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.14/-1.24 |

**Table S8** Bond lengths [Å] for $[N(CH_3)_4]_2GeF_6:Mn^{4+}$ at 150 K ($NMe_4GeF_6$ 150K).

| | |
|---|---|
| C1—N1 | 1.493(4) |
| C2—N1 | 1.481(7) |
| N1—C1[1] | 1.493(4) |
| N1—C1[2] | 1.493(4) |
| F1—Ge1 | 1.784(2) |
| Ge1—F1[3] | 1.784(2) |
| Ge1—F1[4] | 1.784(2) |
| Ge1—F1[5] | 1.784(2) |
| Ge1—F1[6] | 1.784(2) |
| Ge1—F1[7] | 1.784(2) |

[1]1-Y,1+X-Y,+Z; [2]+Y-X,1-X,+Z; [3]4/3-Y+X,2/3+X,2/3-Z; [4]2-Y,2+X-Y,+Z; [5]4/3-X,8/3-Y,2/3-Z; [6]+Y-X,2-X,+Z; [7]-2/3+Y,2/3-X+Y,2/3-Z

**Table S9** Bond Angles [°] for $[N(CH_3)_4]_2GeF_6:Mn^{4+}$ at 150 K ($NMe_4GeF_6$ 150K).

| Bond | Angle/ ° | Bond | Angle/ ° |
|---|---|---|---|
| C1[1]—N1—C1 | 109.8(2) | F1[5]—Ge1—F1[7] | 90.37(13) |
| C1—N1—C1[2] | 109.8(2) | F1[4]—Ge1—F1 | 180.0 |
| C1[1]—N1—C1[2] | 109.8(2) | F1[5]—Ge1—F1 | 90.37(13) |
| C2—N1—C1[2] | 109.2(2) | F1[4]—Ge1—F1[7] | 89.63(13) |
| C2—N1—C1[1] | 109.2(2) | F1[3]—Ge1—F1 | 89.63(13) |
| C2—N1—C1 | 109.2(2) | F1[6]—Ge1—F1 | 89.63(13) |
| F1[3]—Ge1—F1[4] | 90.37(13) | F1[3]—Ge1—F1[7] | 180.0 |
| F1[4]—Ge1—F1[5] | 89.63(13) | F1[4]—Ge1—F1[6] | 90.37(13) |
| F1[3]—Ge1—F1[5] | 89.63(13) | F1—Ge1—F1[7] | 90.37(13) |
| F1[5]—Ge1—F1[6] | 180.0 | | |
| F1[6]—Ge1—F1[7] | 89.63(13) | | |
| F1[3]—Ge1—F1[6] | 90.37(13) | | |

[1]1-Y,1+X-Y,+Z; [2]+Y-X,1-X,+Z; [3]4/3-Y+X,2/3+X,2/3-Z; [4]4/3-X,8/3-Y,2/3-Z; [5]2-Y,2+X-Y,+Z; [6]-2/3+Y,2/3-X+Y,2/3-Z; [7]+Y-X,2-X,+Z

**Table S10** Crystal data and structure refinement for $[N(CH_3)_4]_2GeF_6:Mn^{4+}$ at 293 K ($NMe_4GeF_6$ 293K).

| Identification code | $NMe_4GeF_6$ 293K |
|---|---|
| Empirical formula | $C_8H_{24}F_6GeN_2$ |
| Formula weight | 334.88 |
| Temperature/K | 292.99(10) |
| Crystal system | cubic |
| Space group | *Fm*-3*m* |
| *a*/Å | 11.2682(18) |
| *b*/Å | 11.2682(18) |
| *c*/Å | 11.2682(18) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1430.8(7) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.555 |
| μ/mm$^{-1}$ | 2.191 |
| F(000) | 688.0 |
| Crystal size/mm$^3$ | 0.06 × 0.05 × 0.04 |
| Radiation | MoKα (λ = 0.71073) |

| | |
|---|---|
| 2Θ range for data collection/° | 6.262 to 57.956 |
| Index ranges | $-11 \leq h \leq 15$, $-5 \leq k \leq 12$, $-14 \leq l \leq 12$ |
| Reflections collected | 610 |
| Independent reflections | 127 [$R_{int}$ = 0.1990, $R_{sigma}$ = 0.0889] |
| Data/restraints/parameters | 127/0/9 |
| Goodness-of-fit on $F^2$ | 1.101 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0862, $wR_2$ = 0.2249 |
| Final R indexes [all data] | $R_1$ = 0.0880, $wR_2$ = 0.2289 |
| Largest diff. peak/hole / e $Å^{-3}$ | 1.06/-0.67 |

**Table S11** Bond lengths [Å] for $[N(CH_3)_4]_2GeF_6:Mn^{4+}$ at 293 K ($NMe_4GeF_6$ 293K)..

| | |
|---|---|
| Ge1—F1 | 1.757(11) |
| Ge1—F1[1] | 1.757(11) |
| Ge1—F1[2] | 1.757(11) |
| Ge1—F1[3] | 1.757(11) |
| Ge1—F1[4] | 1.757(11) |
| Ge1—F1[5] | 1.757(11) |
| N1—C1[6] | 1.498(15) |

| | |
|---|---|
| N1—C1[7] | 1.498(15) |
| N1—C1 | 1.498(15) |
| N1—C1[8] | 1.498(15) |

[1]1-X,1-Y,1-Z; [2]1-Y,1-Z,1-X; [3]1-Z,1-X,1-Y; [4]+Z,+X,+Y; [5]+Y,+Z,+X; [6]3/2-X,3/2-Y,+Z; [7]3/2-X,+Y,3/2-Z; [8]+X,3/2-Y,3/2-Z

**Table 12** Bond Angles[˚] for $[N(CH_3)_4]_2GeF_6:Mn^{4+}$ at 293 K ($NMe_4GeF_6$ 293K).

| **Bond** | **Angle/ ˚** | **Bond** | **Angle/ ˚** |
|---|---|---|---|
| F1—Ge1—F1[1] | 90.0 | F1—Ge1—F1[5] | 90.000(1) |

| | | | |
|---|---|---|---|
| F1[2]—Ge1—F1[3] | 180.0 | F1[1]—Ge1—F1[3] | 90.000(3) |
| F1—Ge1—F1[3] | 90.0 | F1[4]—Ge1—F1[5] | 90.0 |
| F1[4]—Ge1—F1[3] | 90.000(2) | C1[6]—N1—C1[7] | 109.471(2) |
| F1[4]—Ge1—F1[2] | 90.0 | C1[6]—N1—C1 | 109.471(1) |
| F1[2]—Ge1—F1[5] | 90.000(2) | C1[7]—N1—C1[8] | 109.471(1) |
| F1—Ge1—F1[2] | 90.000(2) | C1[8]—N1—C1 | 109.471(2) |
| F1—Ge1—F1[4] | 180.0 | C1[7]—N1—C1 | 109.471(3) |
| F1[1]—Ge1—F1[2] | 90.000(1) | C1[6]—N1—C1[8] | 109.471(5) |
| F1[1]—Ge1—F1[5] | 180.0 | | |
| F1[3]—Ge1—F1[5] | 90.000(1) | | |
| F1[1]—Ge1—F1[4] | 90.000(1) | | |

[1]1-Y,1-Z,1-X; [2]+Z,+X,+Y; [3]1-Z,1-X,1-Y; [4]1-X,1-Y,1-Z; [5]+Y,+Z,+X; [6]3/2-X,3/2-Y,+Z; [7]+X,3/2-Y,3/2-Z; [8]3/2-X,+Y,3/2-Z

**Table S13** Crystal data and structure refinement for $[N(CH_3)_4]_2TiF_6:Mn^{4+}$ at 150 K ($NMe_4TiF_6$ 150K).

| Identification code | $NMe_4TiF_6$ 150K |
|---|---|

| | |
|---|---|
| Empirical formula | $C_8H_{24}F_6N_2Ti$ |
| Formula weight | 310.68 |
| Temperature/K | 149.99(10) |
| Crystal system | trigonal |
| Space group | $R\bar{3}$ |
| $a$/Å | 7.8913(2) |
| $b$/Å | 7.8913(2) |
| $c$/Å | 19.9262(7) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 120 |
| $V$/Å$^3$ | 1074.61(7) |
| $Z$ | 3 |
| $\rho_{calc}$g/cm$^3$ | 1.438 |
| μ/mm$^{-1}$ | 0.646 |
| F(000) | 486.0 |
| Crystal size/mm$^3$ | 0.08 × 0.05 × 0.03 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 10.128 to 82.562 |
| Index ranges | -11 ≤ h ≤ 14, -14 ≤ k ≤ 14, -34 ≤ l ≤ 36 |
| Reflections collected | 7932 |
| Independent reflections | 1578 [$R_{int}$ = 0.0324, $R_{sigma}$ = 0.0211] |

| | |
|---|---|
| Data/restraints/parameters | 1578/0/30 |
| Goodness-of-fit on $F^2$ | 1.124 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0241, $wR_2$ = 0.0671 |
| Final R indexes [all data] | $R_1$ = 0.0244, $wR_2$ = 0.0674 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.33/-0.45 |

**Table S14** Bond lengths [Å] for $[N(CH_3)_4]_2TiF_6:Mn^{4+}$ at 150 K ($NMe_4TiF_6$ 150K).

| | |
|---|---|
| Ti1—F1 | 1.862(1) |
| Ti1—F1[1] | 1.862(1) |
| Ti1—F1[2] | 1.862(1) |
| Ti1—F1[3] | 1.862(1) |
| Ti1—F1[4] | 1.862(1) |
| Ti1—F1[5] | 1.862(1) |
| N1—C1 | 1.495(2) |
| N1—C2[6] | 1.494(1) |
| N1—C2[7] | 1.494(1) |
| N1—C2 | 1.494(1) |

[1]1-Y,2+X-Y,+Z; [2]-X,2-Y,1-Z; [3]-1+Y,-X+Y,1-Z; [4]-1+Y-X,1-X,+Z; [5]1-Y+X,1+X,1-

Z; [6]+Y-X,1-X,+Z; [7]1-Y,1+X-Y,+Z

**Table S15** Bond Angles[˚] for $[N(CH_3)_4]_2TiF_6:Mn^{4+}$ at 150 K ($NMe_4TiF_6$ 150K).

| **Bond** | **Angle/ ˚** | **Bond** | **Angle/ ˚** |
|---|---|---|---|
| F1—Ti1—F1[1] | 180.0 | F1[1]—Ti1—F1[4] | 90.06(2) |
| F1[2]—Ti1—F1[3] | 90.06(2) | F1—Ti1—F1[5] | 89.94(2) |
| F1—Ti1—F1[3] | 90.06(2) | F1[1]—Ti1—F1[3] | 89.94(2) |
| F1[4]—Ti1—F1[3] | 89.94(2) | F1[4]—Ti1—F1[5] | 90.06(2) |
| F1[4]—Ti1—F1[2] | 180.0 | C1—N1—C2[6] | 109.38(4) |
| F1[2]—Ti1—F1[5] | 89.94(2) | C2—N1—C1 | 109.38(4) |
| F1—Ti1—F1[2] | 90.06(2) | C2[7]—N1—C1 | 109.38(4) |
| F1—Ti1—F1[4] | 89.94(2) | C2—N1—C2[6] | 109.56(4) |
| F1[1]—Ti1—F1[2] | 89.94(2) | C2[7]—N1—C1[6] | 109.56(4) |
| F1[1]—Ti1—F1[5] | 90.06(2) | C2—N1—C1[7] | 109.56(4) |

| | |
|---|---|
| F1[3]—Ti1—F1[5] | 180.0 |

[1]-X,2-Y,1-Z; [2]-1+Y-X,1-X,+Z; [3]1-Y,2+X-Y,+Z; [4]1-Y+X,1+X,1-Z; [5]-1+Y,-X+Y,1-Z; [6]+Y-X,1-X,+Z; [7]1-Y,1+X-Y,+Z

**Table S16** Crystal data and structure refinement for $[N(CH_3)_4]_2TiF_6$:$Mn^{4+}$ at 293 K ($NMe_4TiF_6$ 293K).

| Identification code | $NMe_4TiF_6$ 293K |
|---|---|
| Empirical formula | $C_8H_{24}F_6N_2Ti$ |
| Formula weight | 310.24 |
| Temperature/K | 293.00(10) |
| Crystal system | cubic |
| Space group | *Fm*-3*m* |
| *a*/Å | 11.372(3) |
| *b*/Å | 11.372(3) |
| *c*/Å | 11.372(3) |
| *α*/° | 90 |

| | |
|---|---|
| $\beta$/° | 90 |
| $\gamma$/° | 90 |
| Volume/Å$^3$ | 1470.8(13) |
| $Z$ | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.401 |
| $\mu$/mm$^{-1}$ | 0.630 |
| F(000) | 648.0 |
| Crystal size/mm$^3$ | 0.06 × 0.04 × 0.03 |
| Radiation | MoKα ($\lambda$ = 0.71073) |
| 2Θ range for data collection/° | 6.206 to 60.512 |
| Index ranges | $-7 \leq h \leq 14$, $-13 \leq k \leq 3$, $-12 \leq l \leq 8$ |
| Reflections collected | 399 |
| Independent reflections | 131 [$R_{int}$ = 0.1075, $R_{sigma}$ = 0.0677] |
| Data/restraints/parameters | 131/0/10 |
| Goodness-of-fit on F$^2$ | 1.125 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0983, $wR_2$ = 0.2421 |
| Final R indexes [all data] | $R_1$ = 0.1081, $wR_2$ = 0.2547 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.69/-0.60 |

**Table S17** Bond lengths [Å] for $[N(CH_3)_4]_2TiF_6:Mn^{4+}$ at 293 K ($NMe_4TiF_6$ 293K).

| | |
|---|---|
| Ti1—F1 | 1.823(8) |
| Ti1—F1[1] | 1.823(8) |
| Ti1—F1[2] | 1.823(8) |
| Ti1—F1[3] | 1.823(8) |
| Ti1—F1[4] | 1.823(8) |
| Ti1—F1[5] | 1.823(8) |
| N1—C1 | 1.492(9) |
| N1—C1[6] | 1.492(9) |
| N1—C1[7] | 1.492(9) |
| N1—C1[8] | 1.492(9) |

[1]1-Z,1-X,1-Y; [2]1-Y,1-Z,1-X; [3]+Y,+Z,+X; [4]+Z,+X,+Y; [5]1-X,1-Y,1-Z; [6]+X,3/2-Y,3/2-Z; [7]3/2-X,3/2-Y,+Z; [8]3/2-X,+Y,3/2-Z

**Table 18** Bond Angles[˚] for$[N(CH_3)_4]_2TiF_6:Mn^{4+}$ at 293 K ($NMe_4TiF_6$ 293K).

| **Bond** | **Angle/ ˚** | **Bond** | **Angle/ ˚** |
|---|---|---|---|
| F1—Ti1—$F1^1$ | 90.000(1) | $F1^1$—Ti1—$F1^5$ | 90.000(2) |
| $F1^2$—Ti1—$F1^3$ | 180.0 | $F1^2$—Ti1—$F1^4$ | 90.000(1) |
| $F1^3$—Ti1—$F1^4$ | 90.000(1) | $F1^1$—Ti1—$F1^3$ | 90.000(1) |
| $F1^5$—Ti1—$F1^3$ | 90.000(2) | F1—Ti1—$F1^3$ | 90.000(1) |
| $F1^1$—Ti1—$F1^4$ | 180.0 | $C1^6$—N1—$C1^7$ | 109.5 |
| $F1^5$—Ti1—$F1^4$ | 90.000(1) | $C1^7$—N1—$C1^8$ | 109.471(2) |
| F1—Ti1—$F1^2$ | 90.000(2) | $C1^6$—N1—$C1^8$ | 109.471(2) |
| F1—Ti1—$F1^5$ | 180.0 | $C1^7$—N1—C1 | 109.5 |
| $F1^1$—Ti1—$F1^2$ | 90.0 | $C1^6$—N1—C1 | 109.471(3) |
| F1—Ti1—$F1^4$ | 90.000(1) | $C1^8$—N1—C1 | 109.5 |
| $F1^5$—Ti1—$F1^2$ | 90.000(1) | | |

$^1$1-Y,1-Z,1-X; $^2$+Z,+X,+Y; $^3$1-Z,1-X,1-Y; $^4$+Y,+Z,+X; $^5$1-X,1-Y,1-Z; $^6$+X,3/2-Y,3/2-Z; $^7$3/2-X,+Y,3/2-Z; $^8$3/2-X,3/2-Y,+Z

**Table S19** Quantum efficiency values and decay times of $[N(CH_3)_4]_2XF_6:Mn^{4+}$

| Sample | IQE (%) | EQE (%) | Time (ms) |
|---|---|---|---|
| $[N(CH_3)_4]_2SiF_6:Mn^{4+}$ | 86.0 | 67.6 | 2.43 |
| $[N(CH_3)_4]_2GeF_6:Mn^{4+}$ | 84.1 | 70.5 | 1.73 |
| $[N(CH_3)_4]_2TiF_6:Mn^{4+}$ | 82.0 | 73.0 | 1.50 |

**Table S20** Performance of white LEDs.

| White LED | CCT (K) | Ra | LE (lm/W) | CIE (x, y) |
|---|---|---|---|---|
| I | 3642 | 95.3 | 88.2 | 0.390, 0.365 |
| II | 4079 | 88.7 | 80.7 | 0.367, 0.335 |
| III | 3607 | 95.1 | 74 | 0.392, 0.367 |
| IV | 4704 | 70.4 | 133.5 | 0.361, 0.405 |

## References


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