# 4f→3d Sensitization: Luminescent $Eu^{II}$-$Mn^{II}$ heteronuclear complex with a near-unity quantum yield

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**Content**

## 1. Experimental Details

### Chemicals and Synthesis

The starting materials $EuBr_2$ (99.99%, Aladdin), $SrBr_2$ (anhydrous, 99.9%, 3AChem), $MnBr_2$ (99%, Macklin), $ZnBr_2$ (98%, D&B) and N2O6 ligand (98%, D&B) were commercially available and were used as received.

The synthesis and pretreatment for characterization of complexes were conducted in dry glovebox filled with nitrogen. n-Hexane was distilled using Na and NaH under a nitrogen atmosphere. Extra dry solvents such as methanol, ethanol, and acetonitrile were degassed before used in glovebox.

**Synthesis of [Eu(N2O6)Br]Br**. N2O6 (217.9 mg, 0.579 mmol, dissolved in 1.0 mL methanol) was added into the solution of $EuBr_2$ (168.9 mg, 0.542 mmol, dissolved in 2.0 mL methanol) filtered by a syringe-driven filter (0.22 μm, nylon) under magnetic stirring. After this colorless mixture was stirred for 12 h, the solvent was removed under reduced pressure. The residues were treated with 1 mL acetonitrile. The solvent was removed under reduced pressure again to get white precipitates. The precipitates were washed by n-hexane to yield [Eu(N2O6)Br]Br as a white solid (310.1 mg, 83%). Elemental analysis calcd (%) for $C_{18}H_{36}Br_2EuN_2O_6$: C 31.41, H 5.27, N 4.07; found: C 31.26, H 5.38, N 4.04.

**Synthesis of [Eu(N2O6)]$MnBr_4$**. [Eu(N2O6)Br]Br (100.1 mg, 0.145 mmol, dissolved in 0.8 mL methanol) and $MnBr_2$ (31.2 mg, 0.145 mmol, dissolved in 0.6 mL methanol) were mixed well after filtered by a syringe-driven filter (0.22 μm, nylon). Pale green crystals were obtained as the evaporation of solvent without perturbance. These crystals were crushed and washed by n-hexane to yield [Eu(N2O6)]$MnBr_4$ as a pale green solid (95.7 mg, 68%). Elemental analysis calcd (%) for $C_{20}H_{44}Br_4EuMnN_2O_8$: C 24.84, H 4.59, N 2.90; found: C 24.52, H 4.14, N 3.02.

**Synthesis of [Sr(N2O6)]$MnBr_4$**. [Sr(N2O6)]$MnBr_4$ was prepared following similar procedures of [Eu(N2O6)]$MnBr_4$. Its Sr-containing precursor was prepared from N2O6 (100.0 mg, 0.266 mmol) and $SrBr_2$ (58.2 mg, 0.235 mmol) with a yield of 67%. After the reaction of the Sr-containing precursor (89.9 mg, 0.144 mmol) and $MnBr_2$ (30.9 mg, 0.144 mmol), [Sr(N2O6)]$MnBr_4$ was obtained as a pale green solid (94.7 mg, 73%). Elemental analysis calcd (%) for $C_{20}H_{44}Br_4MnN_2O_8Sr$: C 26.61, H 4.91, N 3.10; found: C 26.77, H 4.45, N 3.34.

**Synthesis of [Eu(N2O6)]$ZnBr_4$**. [Eu(N2O6)]$ZnBr_4$ was prepared following similar procedures of [Eu(N2O6)]$MnBr_4$, but instead [Eu(N2O6)Br]Br (98.8 mg, 0.144 mmol) and $ZnBr_2$ (32.7 mg, 0.145 mmol) were used. [Eu(N2O6)]$ZnBr_4$ was obtained as a white solid (56.6 mg, 43%). Elemental analysis calcd (%) for $C_{18}H_{36}Br_4EuN_2O_6Zn$: C 23.67, H 3.97, N 3.07; found: C 23.84, H 3.98, N 2.88.

**Fabrication of pc-LEDs**. The pc-LEDs were fabricated from violet InGaN chip (405 nm, 1 W, 3 V, Shenzhen Fangpu Photoelectric Co., Ltd., China) in a glovebox. Firstly, silicone resin (1610A/B, Asada Chemical Industry Co., Ltd., Japan) was prepared by mixing the A/B components at the ratio of 1:1. Then, the powder sample of [Eu(N2O6)]$MnBr_4$ was fully blended with silicone resin to get the light-converting adhesive. After several drops of this adhesive were coated on the LED chip, the whole device was heated at 150 ℃ for 1 h to make the resin solidify. The control devices (LEDs with [Sr(N2O6)]$MnBr_4$ coated) were fabricated in the same way and equivalent doping ratios.

## 2. General Characterization

**Elemental analysis**

Elemental analyses were performed on a VARIO EL analyzer (GmbH, Hanau, Germany).

**Single crystal structure measurements**

The single crystal X-ray diffraction (SCXRD) data were collected on a Rigaku Mercury CCD diffractometer. The radiation used in the SCXRD analysis is the graphite-monochromated Mo Kα emission line (λ= 0.71069 Å). SCXRD data were collected by using the CrystalClear software. Structural refinements were conducted with SHELXL-97 or SHELXL-2013 software.

**Sample preparation method for photophysical properties test**

All solid samples were encapsulated between two quartz plates (20×20×1 mm) by paraffin. The commercially available paraffin was further purified by oxidation using $KMnO_4$ and activated carbon to remove fluorescent whitening agents. All solution samples were protected by capped cuvettes under $N_2$ atmosphere and their concentrations were around $10^{-3}$ mol·$L^{-1}$. All measurements were performed under room temperature except the temperature-dependent spectra.

**State and transient PL**

Fluorescence and transient PL decay spectra were measured on an Edinburgh Analytical Instruments FLS980 spectrophotometer with Xe lamp, microsecond lamp, and pulsed lasers (Edinburgh). The transient PL decay spectra data were analyzed by tail fit of the decay profile using a software package provided by Edinburgh Instruments. The quality of the fits was evidenced by appropriate $\chi^2$ values ($0.8 < \chi^2 < 1.3$).

**Temperature-dependent PL**

Temperature-dependent fluorescence and transient PL decay spectra were measured on the same Edinburgh FLS980 spectrophotometer and an Oxford temperature controlling system was employed to change the temperature from 5 K to 303 K.

**Time resolved emission spectra (TRES)**

TRES were measured on an Edinburgh Analytical Instruments FLS1000 spectrophotometer with a picosecond diode laser (Taiko, 375 nm, 100 Hz). The detecting range was 20 μs with 1000 channels (10 ns per channel). The raw data were sliced by 10 ns to give spectra at different time. Then, the time dimension was shifted to make sure that '0 ns' corresponds to the spectrum with maximum intensity.

**UV−Vis absorption**

UV-vis absorption spectra were obtained from a Shimadzu UV- 3600Plus UV-VIS-NIR spectrometer. Solution samples were tested under a double optical path model. Solid samples were tested under a single path model with an integrating sphere detector.

**PLQY Test**

PLQYs were measured in Hamamatsu C9920-02 absolute quantum yield measurement system with an integrating sphere. The relative error of PLQY test is around ±5%.

**Test of pc-LEDs**

The photoelectric properties of pc-LEDs, including the emission spectrum, luminous efficiency, external quantum efficiency (EQE) and commission internationale de l´eclairage (CIE) color coordinates, were measured by using computer-controlled Keithley 2400 source meter and Hamamatsu C9920-12 external quantum efficiency measurement system with an integrating sphere and a photonic multichannel analyzer. The tests were conducted in a glove box filled with nitrogen.

## 3. Supplementary Data

**Table S1.** Crystallographic data of [Eu(N2O6)Br]Br. Further details of the crystal structure investigation may be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CCDC 2165321.

| Complex | [Eu(N2O6)Br]Br |
|---|---|
| Formula | $C_{18}H_{36}Br_2EuN_2O_6$ |
| Mw | 688.27 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12$ |
| $a$ (Å) | 13.6795(3) |
| $b$ (Å) | 17.7174(3) |
| $c$ (Å) | 9.9143(2) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 2402.88(8) |
| $Z$ | 4 |
| $T$ (K) | 179.99(10) |
| $\theta$ range (°) | 2.3600 – 29.2230 |
| $d_{calc}$ (g·cm$^{-3}$) | 1.903 |
| F (000) | 1356 |
| Crystal size (mm) | 0.18 × 0.16 × 0.09 |
| Absorp. coeff. (mm$^{-1}$) | 5.970 |
| Index range | $-18 \le h \le 11$<br>$-24 \le k \le 20$<br>$-13 \le l \le 9$ |
| Reflns collected | 11809 ($R_{int}$ = 0.0213) |
| Indep. reflns | 5554 |
| Refns obs. [$I > 2\sigma(I)$] | 5294 |
| data/restr/paras | 5554/0/263 |
| GOF | 1.055 |
| $R_1$/$wR_2$ [$I > 2\sigma(I)$] | 0.0196/0.0382 |
| $R_1$/$wR_2$ (all data) | 0.0218/0.0387 |
| Largest diff. peak & hole (e/Å$^3$) | 0.590/-0.560 |

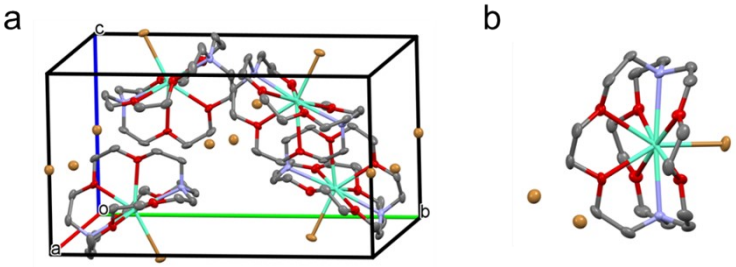


**Figure S1.** Single-crystal structures showing as ellipsoids at the 50% probability level for [Eu(N2O6)Br]Br. All the hydrogens are omitted for clarification. Atom notation: C grey, Br brown, Eu cyan, N blue, O red. a) Unit cell; b) Molecular structure (asymmetric unit).

**Table S2.** Crystallographic data of [Eu(N2O6)]$MnBr_4$. Further details of the crystal structure investigation may be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CCDC 2164366.

| Complex | [Eu(N2O6)]$MnBr_4$ |
|---|---|
| Formula | $C_{20.65}H_{45.30}Br_4EuMnN_2O_8$ |
| Mw | 976.23 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| *a* (Å) | 16.7005(10) |
| *b* (Å) | 11.9358(4) |
| *c* (Å) | 16.9034(8) |
| *α* (°) | 90 |
| *β* (°) | 108.602(6) |
| *γ* (°) | 90 |
| *V* (Å$^3$) | 3193.4(3) |
| *Z* | 4 |
| *T* (K) | 180.00(10) |
| *θ* range (°) | 2.5030 - 30.5930 |
| $d_{calc}$ (g·cm$^{-3}$) | 2.031 |
| F (000) | 1901 |
| Crystal size (mm) | 0.33 × 0.14 × 0.13 |
| Absorp. coeff. (mm$^{-1}$) | 7.388 |
| Index range | -18 ≤ h ≤ 19<br>-11 ≤ k ≤ 14<br>-19 ≤ l ≤ 20 |
| Reflns collected | 20114 ($R_{int}$ = 0.0305) |
| Indep. reflns | 5639 |
| Refns obs. [$I > 2\sigma(I)$] | 4740 |
| data/restr/paras | 5639/125/360 |
| GOF | 1.065 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.0621/0.1473 |
| $R_1/wR_2$ (all data) | 0.0735/0.1524 |
| Largest diff. peak & hole (e/Å$^3$) | 2.835/-3.251 |

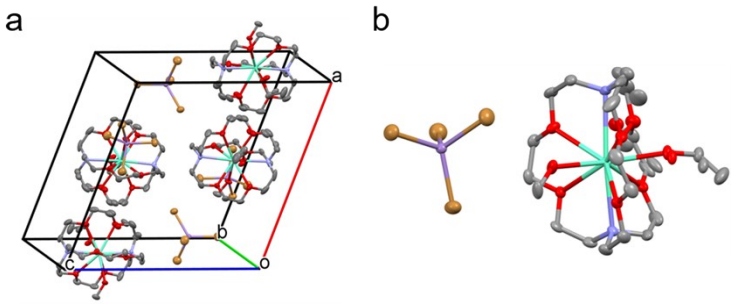


**Figure S2.** Single-crystal structures showing as ellipsoids at the 50% probability level for [Eu(N2O6)]$MnBr_4$. Most of the hydrogens are omitted for clarification. Atom notation: C grey, Br brown, Eu cyan, Mn purple, N blue, O red. a) Unit cell; b) Molecular structure (asymmetric unit).

**Table S3.** Crystallographic data of [Sr(N2O6)]$MnBr_4$. Further details of the crystal structure investigation may be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CCDC 2164368.

| Complex | [Sr(N2O6)]$MnBr_4$ |
|---|---|
| Formula | $C_{20}H_{45.11}Br_{2.89}MnN_2O_{9.11}Sr$ |
| Mw | 832.95 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 11.5435(4) |
| $b$ (Å) | 20.2186(5) |
| $c$ (Å) | 13.5459(5) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 91.420(3) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 3160.55(18) |
| $Z$ | 4 |
| $T$ (K) | 180.00(10) |
| $\theta$ range (°) | 2.4780 - 27.5770 |
| $d_{calc}$ (g·cm$^{-3}$) | 1.751 |
| F (000) | 1665 |
| Crystal size (mm) | 0.18 × 0.04 × 0.01 |
| Absorp. coeff. (mm$^{-1}$) | 5.785 |
| Index range | $-13 \le h \le 14$<br>$-28 \le k \le 28$<br>$-19 \le l \le 17$ |
| Reflns collected | 23695 ($R_{int}$ = 0.0451) |
| Indep. reflns | 8232 |
| Refns obs. [$I > 2\sigma(I)$] | 5215 |
| data/restr/paras | 8232/66/422 |
| GOF | 1.021 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.0482/0.0945 |
| $R_1/wR_2$ (all data) | 0.0971/0.1083 |
| Largest diff. peak & hole (e/Å$^3$) | 0.761/-0.625 |

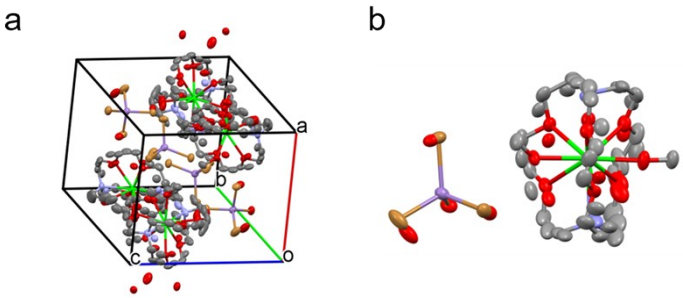


**Figure S3.** Single-crystal structures showing as ellipsoids at the 50% probability level for [Sr(N2O6)]$MnBr_4$. Most of the hydrogens are omitted for clarification. Atom notation: C grey, Br brown, Sr green, Mn purple, N blue, O red. a) Unit cell; b) Molecular structure (asymmetric unit).

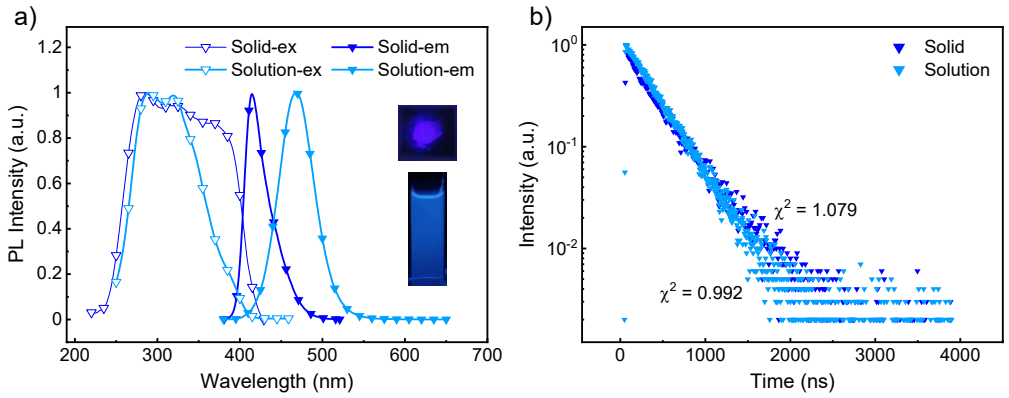


**Figure S4.** a) PL spectra and b) transient decay spectra of [Eu(N2O6)Br]Br in solid state ($\lambda_{ex}$ = 365 nm) and in $1\times10^{-3}$ M methanol ($\lambda_{ex}$ = 320 nm). Inset: photographs under 365 nm irradiation.

**Table S4.** Wavelength-dependent PLQY data of [Eu(N2O6)]$MnBr_4$ in solid state

| $\lambda_{ex}$ (nm) | 270 | 280 | 290 | 300 | 310 | 320 | 330 | 340 |
|---|---|---|---|---|---|---|---|---|
| PLQY (%) | ~100 | ~100 | 97 | 95 | 95 | 93 | 91 | 89 |
| $\lambda_{ex}$ (nm) | 350 | 360 | 370 | 380 | 390 | 400 | 410 | 420 |
| PLQY (%) | 87 | 88 | 87 | 85 | 84 | 86 | 84 | 84 |

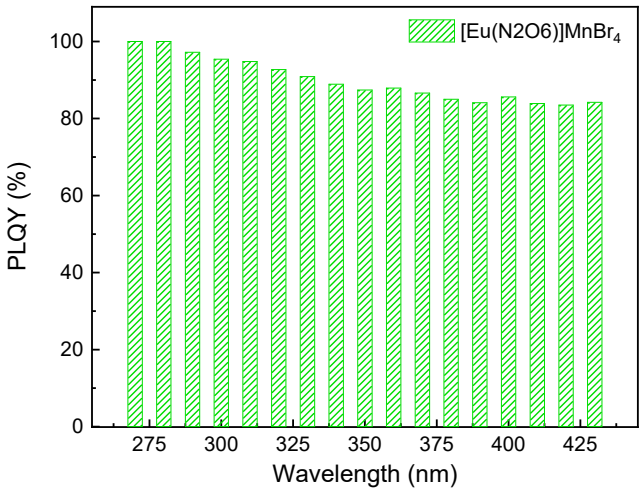


**Figure S5.** Wavelength-dependent PLQY data of [Eu(N2O6)]$MnBr_4$ in solid state.

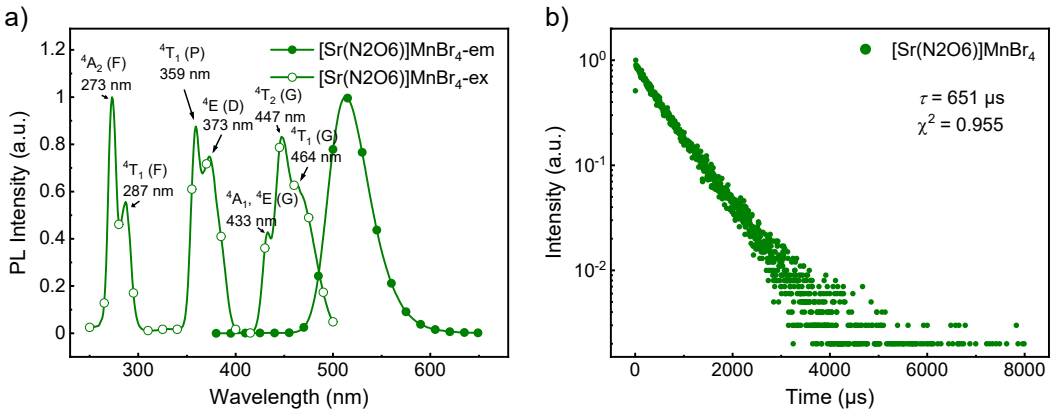


**Figure S6.** a) PL spectra and b) transient decay spectra of [Sr(N2O6)]$MnBr_4$ in solid state ($\lambda_{ex}$ = 450 nm).

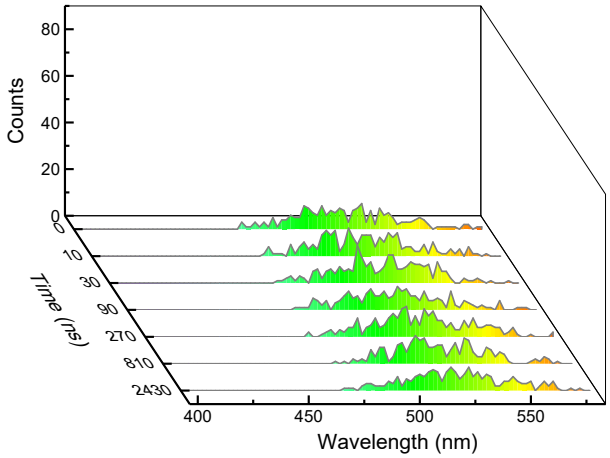


**Figure S7.** Time-resolved emission spectra of [Sr(N2O6)]$MnBr_4$ ($\lambda_{ex}$ = 375 nm, 10 ns per slice) in solid state.

**Table S5.** Crystallographic data of [Eu(N2O6)]$ZnBr_4$. Further details of the crystal structure investigation may be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CCDC 2220493.

| Complex | [Eu(N2O6)]$ZnBr_4$ |
|---|---|
| Formula | $C_{20}H_{44}Br_4EuN_2O_8Zn$ |
| Mw | 977.54 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| *a* (Å) | 14.04743(16) |
| *b* (Å) | 14.65564(16) |
| *c* (Å) | 31.3669(4) |
| *α* (°) | 90 |
| *β* (°) | 102.7436(12) |
| *γ* (°) | 90 |
| *V* (Å$^3$) | 6298.55(13) |
| *Z* | 4 |
| *T* (K) | 180.00(10) |
| *θ* range (°) | 1.486 - 29.768 |
| $d_{calc}$ (g·cm$^{-3}$) | 2.062 |
| F (000) | 3800 |
| Crystal size (mm) | 0.12 × 0.06 × 0.06 |
| Absorp. coeff. (mm$^{-1}$) | 7.852 |
| Index range | -17 ≤ h ≤ 19<br>-19 ≤ k ≤ 20<br>-42 ≤ l ≤ 42 |
| Reflns collected | 81025 ($R_{int}$ = 0.0364) |
| Indep. reflns | 16468 |
| Refns obs. [$I > 2\sigma(I)$] | 13772 |
| data/restr/paras | 16468/9/663 |
| GOF | 1.017 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.0286/0.0524 |
| $R_1/wR_2$ (all data) | 0.0405/0.0551 |
| Largest diff. peak & hole (e/Å$^3$) | 0.928/-0.958 |

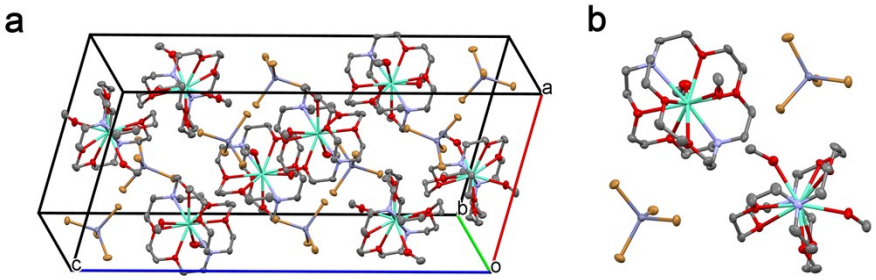


**Figure S8.** Single-crystal structures showing as ellipsoids at the 50% probability level for [Eu(N2O6)]$ZnBr_4$. Most of the hydrogens are omitted for clarification. Atom notation: C grey, Br brown, Eu cyan, Zn blue-grey, N blue, O red. a) Unit cell; b) Molecular structure (asymmetric unit).

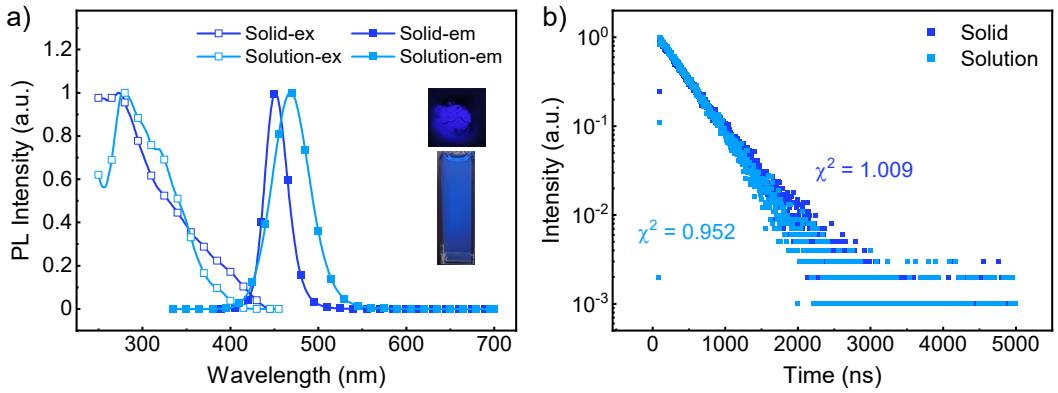


**Figure S9.** a) PL spectra and b) transient decay spectra of [Eu(N2O6)]$ZnBr_4$ in solid state ($\lambda_{ex}$ = 375 nm) and in $1\times10^{-3}$ M methanol ($\lambda_{ex}$ = 320 nm). Inset: photographs under 365 nm irradiation.

**Table S6.** The summary of excitation wavelengths for PLQY testing of the three complexes in Table 2

| Complex | state | $\lambda_{ex}$ (nm) |
|---|---|---|
| [Eu(N2O6)Br]Br | powder | 380 |
| | solution | 280 |
| [Eu(N2O6)]$MnBr_4$ | powder | 280 |
| | solution | 280 |
| [Sr(N2O6)]$MnBr_4$ | powder | 273 |
| [Eu(N2O6)]$ZnBr_4$ | powder | 280 |
| | solution | 280 |

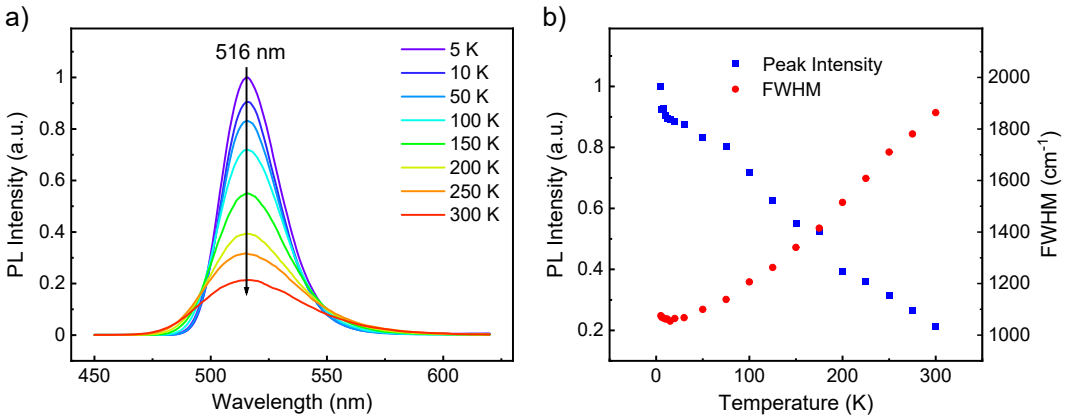


**Figure S10.** Temperature-dependent photophysical properties of [Eu(N2O6)]$MnBr_4$ in solid state ($\lambda_{ex}$ = 365 nm): a) emission spectra, and b) peak intensity and FWHM evolution.

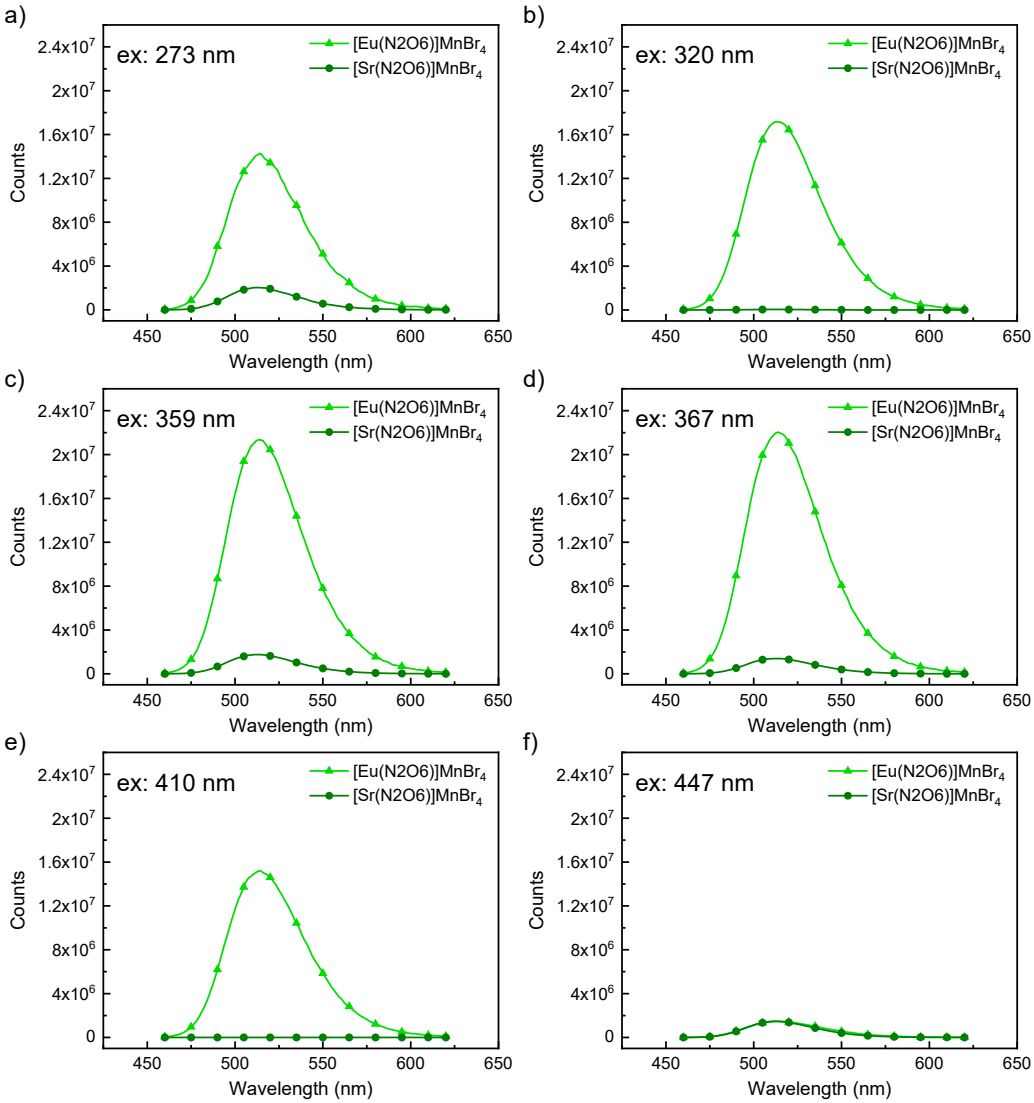


**Figure S11.** Emission spectra at a) 273 nm, b) 320 nm, c) 359 nm, d) 367 nm, e) 410 nm and f) 447 nm excitation of $[Eu(N2O6)]MnBr_4$ and $[Sr(N2O6)]MnBr_4$. Both samples were tested under the same excitation intensity and system parameters. The spectra of $[Eu(N2O6)]MnBr_4$ have been corrected by assuming the peak counts of $[Sr(N2O6)]MnBr_4$ and $[Eu(N2O6)]MnBr_4$ are the same at 447 nm excitation.

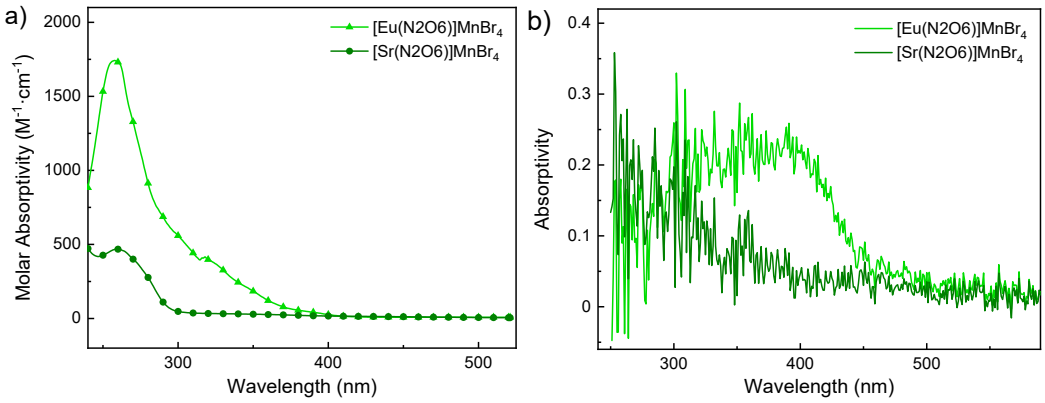


**Figure S12.** UV-vis absorption spectra of a) solution and b) solid samples of $[Eu(N2O6)]MnBr_4$ and $[Sr(N2O6)]MnBr_4$. The solution spectra were tested in methanol with a concentration of $1\times10^{-3}$ M. For solid samples, both 10 mg of powders were encapsulated between two quartz plates and compacted to a thin layer with areas over 1 $cm^2$. The spot of incident light beam is within the center of sample layers to ensure excitation repeatability.

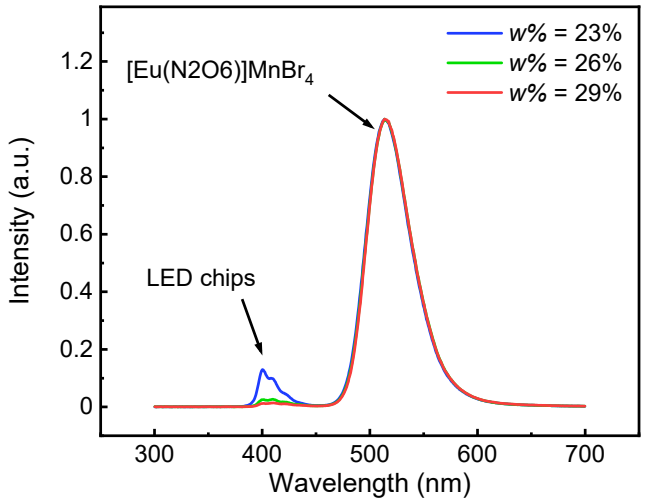


**Figure S13.** Emission spectra of pc-LEDs with $[Eu(N2O6)]MnBr_4$ coated at different doping ratios (*w%* = $m_{sample}$ / $m_{resin}$) under 6 mA forward-bias current.

**Table S7.** The electroluminescence performance data of the pc-LEDs under 6 mA forward-bias current.

| Coating | *w%* (%) | Luminous efficiency (lm/W) | EQE (%) | CIE x | CIE y |
|---|---|---|---|---|---|
| **blank** | - | 1.40 | 14.0 | 0.204 | 0.077 |
| **$[Eu(N2O6)]MnBr_4$** | 23 | 42.6 | 12.3 | 0.180 | 0.653 |
| | 26 | 42.0 | 11.6 | 0.184 | 0.667 |
| | 29 | 37.9 | 10.4 | 0.184 | 0.671 |
| **$[Sr(N2O6)]MnBr_4$** | 26 | 1.63 | 5.77 | 0.222 | 0.179 |