



Supplementary Materials

Ligand Engineering Triggered Efficiency Tunable Emission in Zero-Dimensional Manganese Hybrids for White Light-Emitting Diodes

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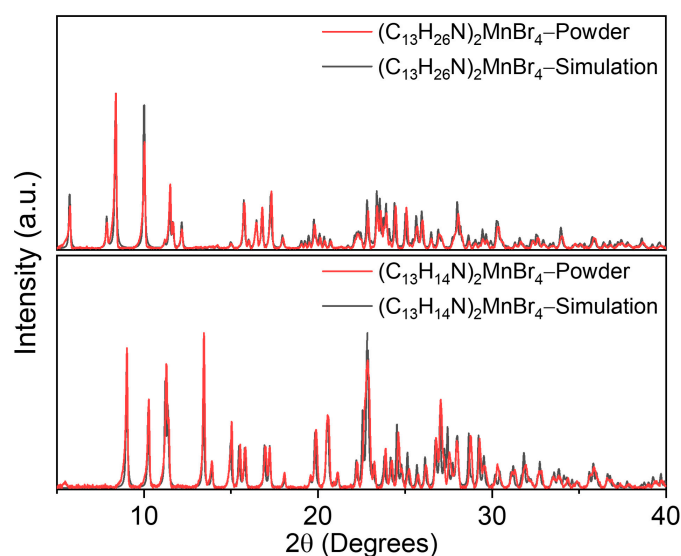


Figure S1. PXRD patterns and standard diffraction pattern of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$.

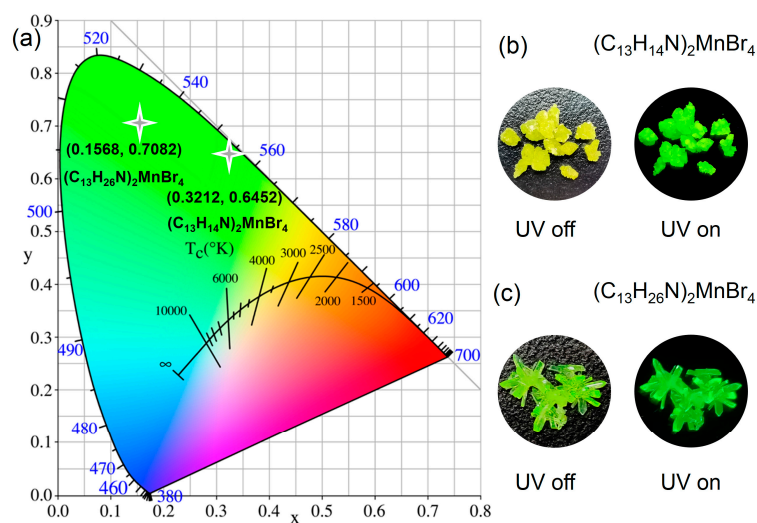


Figure S2. (a) The CIE chromaticity diagrams of $(\text{C}_{13}\text{H}_{14}\text{N})_2\text{MnBr}_4$ and $(\text{C}_{13}\text{H}_{26}\text{N})_2\text{MnBr}_4$. (b, c) The photographs of $(\text{C}_{13}\text{H}_{14}\text{N})_2\text{MnBr}_4$ (top) and $(\text{C}_{13}\text{H}_{26}\text{N})_2\text{MnBr}_4$ (bottom) with UV off and on.

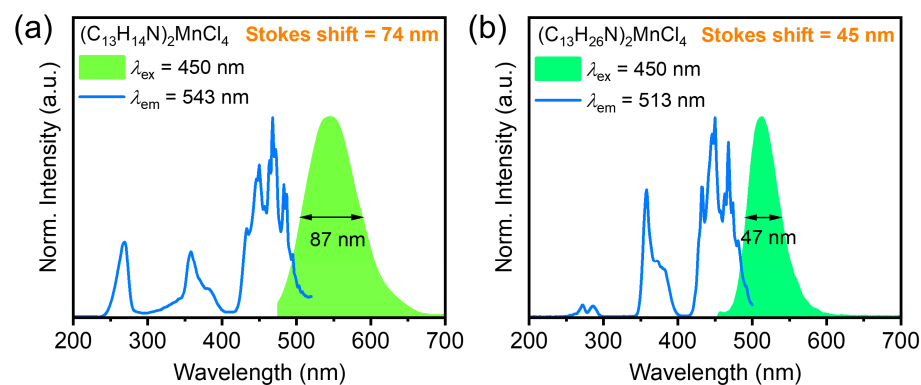


Figure S3. Normalized PLE and PL spectra of (a) $(\text{C}_{13}\text{H}_{14}\text{N})_2\text{MnCl}_4$ and (b) $(\text{C}_{13}\text{H}_{26}\text{N})_2\text{MnCl}_4$.

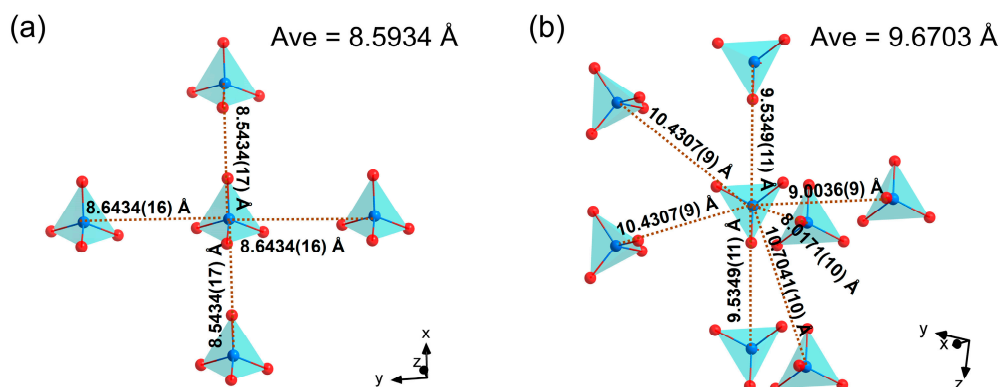


Figure S4. The schematic diagrams of Mn...Mn distance in (a) $(\text{C}_{13}\text{H}_{14}\text{N})_2\text{MnBr}_4$ and (b) $(\text{C}_{13}\text{H}_{26}\text{N})_2\text{MnBr}_4$.

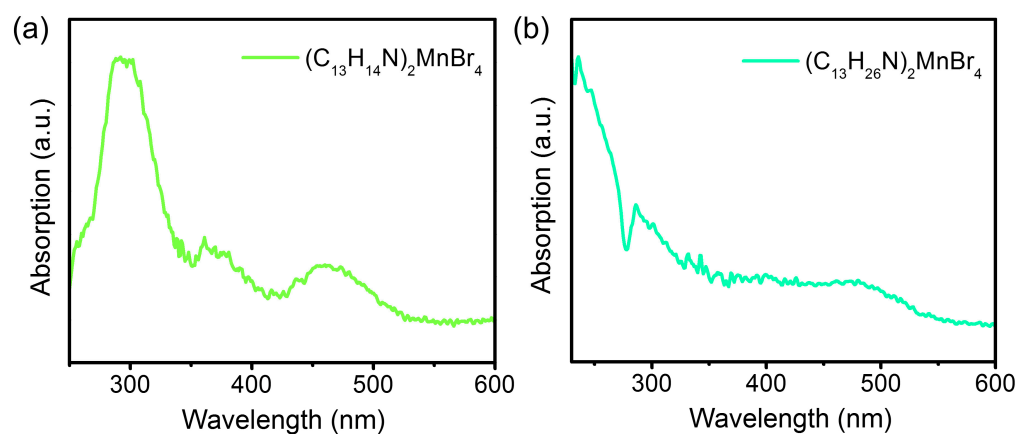


Figure S5. Absorption spectra of (a) $(C_{13}H_{14}N)_2MnBr_4$ and (b) $(C_{13}H_{26}N)_2MnBr_4$.

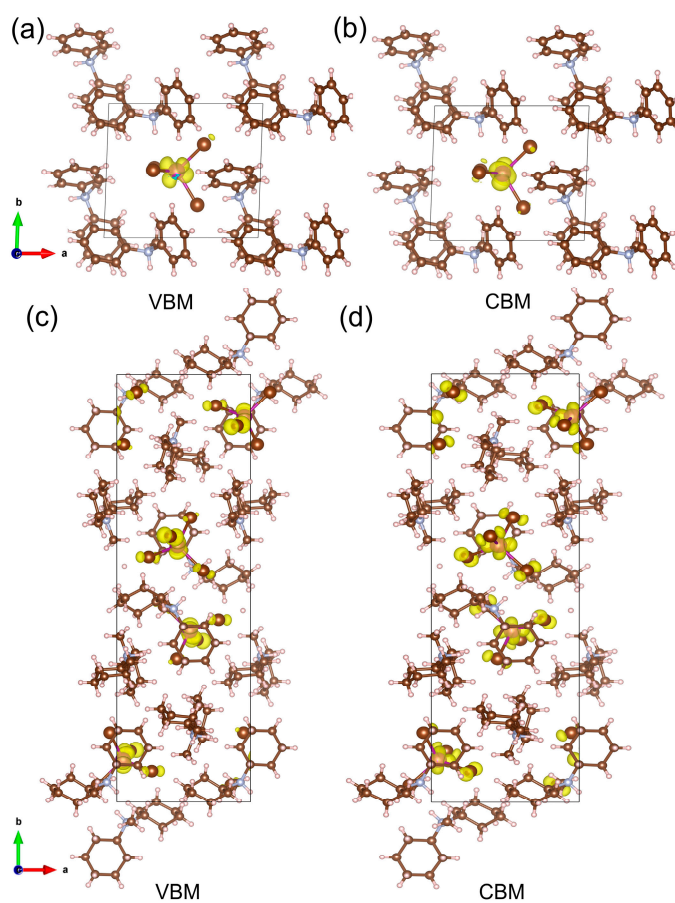


Figure S6. VBM- and CBM-associated charge densities of (a, b) $(C_{13}H_{14}N)_2MnBr_4$ and (c, d) $(C_{13}H_{26}N)_2MnBr_4$.

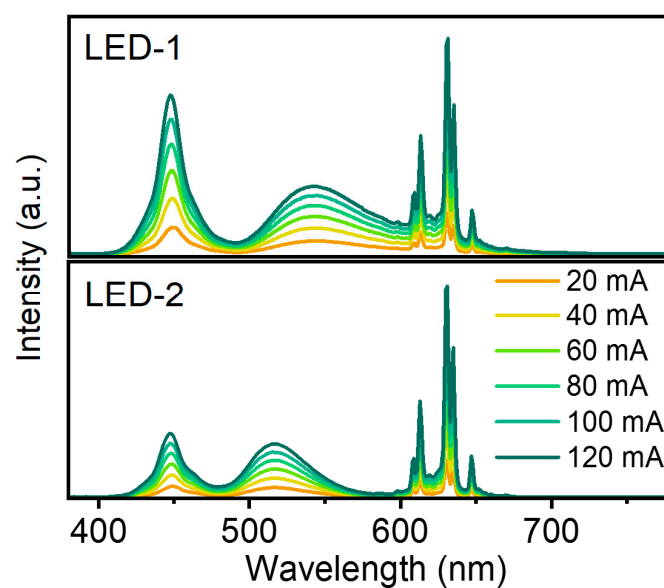


Figure S7. PL spectra of the WLED devices excited at different current (20–120 mA).

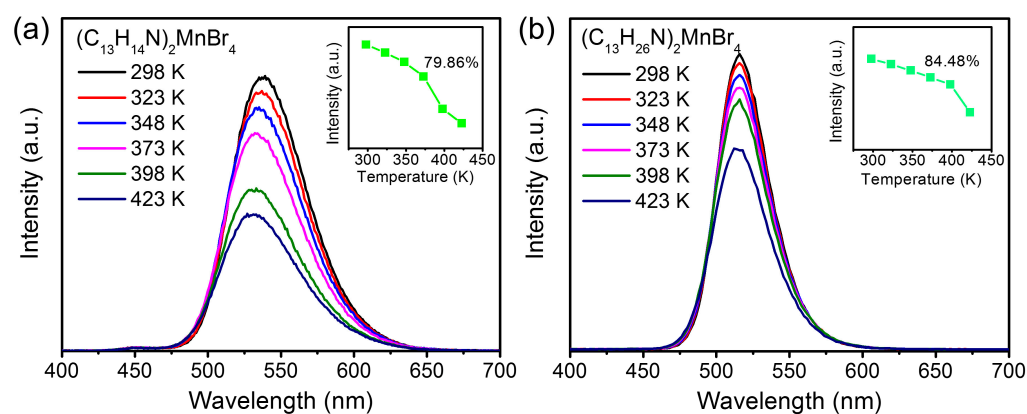


Figure S8. Temperature-dependent PL spectra of (a) $(C_{13}H_{14}N)_2MnBr_4$ and (b) $(C_{13}H_{26}N)_2MnBr_4$ under 450 nm excitation ranging from 298 K to 423 K.

Table S1. The bond length (Å) of (C₁₃H₁₄N)₂MnBr₄ and (C₁₃H₂₆N)₂MnBr₄.

| (C ₁₃ H ₁₄ N) ₂ MnBr ₄ | | | |
|--|-------------|---------------|------------|
| Atom–Atom | Length/Å | Atom–Atom | Length/Å |
| Br (3)–Mn (1) | 2.4915 (13) | C (16)–C (15) | 1.384 (14) |
| Br (1)–Mn (1) | 2.5201 (13) | C (9)–C (8) | 1.369 (14) |
| Br (4)–Mn (1) | 2.5199 (12) | C (9)–C (10) | 1.361 (13) |
| Br (2)–Mn (1) | 2.4829 (13) | C (14)–C (15) | 1.376 (12) |
| N (1)–C (19) | 1.486 (9) | C (6)–C (5) | 1.392 (19) |
| N (1)–C (20) | 1.515 (11) | C (23)–C (22) | 1.398 (13) |
| N (1)–C (21) | 1.496 (9) | C (23)–C (24) | 1.369 (19) |
| N (2)–C (1) | 1.501 (9) | C (11)–C (10) | 1.389 (16) |
| N (2)–C (7) | 1.491 (12) | C (11)–C (12) | 1.37 (2) |
| N (2)–C (8) | 1.479 (9) | C (5)–C (4) | 1.37 (2) |
| C (18)–C (19) | 1.371 (10) | C (8)–C (13) | 1.383 (14) |
| C (18)–C (17) | 1.397 (12) | C (22)–C (21) | 1.375 (10) |
| C (1)–C (2) | 1.332 (13) | C (21)–C (26) | 1.361 (13) |
| C (1)–C (6) | 1.360 (13) | C (26)–C (25) | 1.403 (15) |
| C (19)–C (14) | 1.393 (9) | C (24)–C (25) | 1.369 (18) |
| C (2)–C (3) | 1.403 (13) | C (3)–C (4) | 1.333 (18) |
| C (17)–C (16) | 1.369 (13) | C (13)–C (12) | 1.392 (16) |
| (C ₁₃ H ₂₆ N) ₂ MnBr ₄ | | | |
| Atom–Atom | Length/Å | Atom–Atom | Length/Å |
| Br (01)–Mn (1) | 2.4976 (9) | C (8)–C (13) | 1.516 (11) |
| Br (02)–Mn (1) | 2.5226 (9) | C (8)–C (9) | 1.483 (10) |
| Br (03)–Mn (1) | 2.5099 (9) | C (13)–C (12) | 1.523 (13) |
| Br (04)–Mn (1) | 2.4704 (9) | C (22)–C (23) | 1.522 (11) |
| N (1)–C (14) | 1.510 (6) | C (15)–C (16) | 1.528 (10) |
| N (1)–C (21) | 1.531 (6) | C (19)–C (18) | 1.560 (11) |
| N (1)–C (20) | 1.508 (6) | C (1)–C (2) | 1.559 (15) |
| C (14)–C (15) | 1.513 (8) | C (25)–C (24) | 1.483 (12) |
| C (14)–C (19) | 1.498 (8) | C (24)–C (23) | 1.515 (12) |
| C (21)–C (26) | 1.511 (7) | C (2)–C (3) | 1.476 (17) |
| C (21)–C (22) | 1.489 (8) | C (16)–C (17) | 1.477 (14) |
| C (26)–C (25) | 1.519 (8) | C (10)–C (9) | 1.502 (11) |
| N (2)–C (6) | 1.578 (10) | C (10)–C (11) | 1.494 (15) |
| N (2)–C (8) | 1.460 (9) | C (5)–C (4) | 1.463 (15) |
| N (2)–C (7) | 1.481 (9) | C (18)–C (17) | 1.467 (15) |
| C (6)–C (1) | 1.503 (9) | C (11)–C (12) | 1.469 (15) |
| C (6)–C (5) | 1.487 (10) | C (3)–C (4) | 1.536 (14) |

Table S2. The bond angles (°) of (C₁₃H₁₄N)₂MnBr₄ and (C₁₃H₂₆N)₂MnBr₄.

| (C ₁₃ H ₁₄ N) ₂ MnBr ₄ | | | |
|--|------------|----------------------|------------|
| Atom–Atom–Atom | Angle/° | Atom–Atom–Atom | Angle/° |
| Br (3)–Mn (1)–Br (1) | 108.56 (4) | C (10)–C (9)–C (8) | 118.5 (9) |
| Br (3)–Mn (1)–Br (4) | 110.62 (4) | C (15)–C (14)–C (19) | 117.9 (7) |
| Br (4)–Mn (1)–Br (1) | 110.25 (5) | C (1)–C (6)–C (5) | 118.5 (11) |
| Br (2)–Mn (1)–Br (3) | 117.83 (6) | C (24)–C (23)–C (22) | 120.2 (9) |
| Br (2)–Mn (1)–Br (1) | 106.14 (5) | C (12)–C (11)–C (10) | 119.2 (9) |
| Br (2)–Mn (1)–Br (4) | 103.19 (5) | C (4)–C (5)–C (6) | 119.5 (9) |
| C (19)–N (1)–C (20) | 113.1 (6) | C (9)–C (8)–N (2) | 116.3 (7) |

| | | | |
|----------------------|-----------|----------------------|------------|
| C (19)–N (1)–C (21) | 110.9 (5) | C (9)–C (8)–C (13) | 122.4 (8) |
| C (21)–N (1)–C (20) | 114.2 (6) | C (13)–C (8)–N (2) | 121.3 (9) |
| C (7)–N (2)–C (1) | 111.9 (8) | C (21)–C (22)–C (23) | 118.0 (9) |
| C (8)–N (2)–C (1) | 111.4 (5) | C (9)–C (10)–C (11) | 121.4 (11) |
| C (8)–N (2)–C (7) | 114.8 (7) | C (22)–C (21)–N (1) | 121.2 (7) |
| C (19)–C (18)–C (17) | 119.5 (7) | C (26)–C (21)–N (1) | 116.4 (6) |
| C (2)–C (1)–N (2) | 117.1 (7) | C (26)–C (21)–C (22) | 122.4 (8) |
| C (2)–C (1)–C (6) | 122.7 (8) | C (21)–C (26)–C (25) | 119.0 (9) |
| C (6)–C (1)–N (2) | 120.2 (8) | C (23)–C (24)–C (25) | 121.1 (10) |
| C (18)–C (19)–N (1) | 118.5 (6) | C (4)–C (3)–C (2) | 120.9 (11) |
| C (18)–C (19)–C (14) | 121.4 (7) | C (14)–C (15)–C (16) | 121.6 (8) |
| C (14)–C (19)–N (1) | 120.1 (6) | C (3)–C (4)–C (5) | 120.3 (10) |
| C (1)–C (2)–C (3) | 118.1 (9) | C (24)–C (25)–C (26) | 119.2 (11) |
| C (16)–C (17)–C (18) | 119.9 (8) | C (8)–C (13)–C (12) | 117.7 (12) |
| C (17)–C (16)–C (15) | 119.7 (8) | C (11)–C (12)–C (13) | 120.9 (10) |

(C₁₃H₂₆N)₂MnBr₄

| Atom–Atom–Atom | Angle/° | Atom–Atom–Atom | Angle/° |
|------------------------|------------|----------------------|------------|
| Br (01)–Mn (1)–Br (02) | 108.61 (3) | N (2)–C (8)–C (13) | 110.4 (6) |
| Br (01)–Mn (1)–Br (03) | 107.07 (3) | N (2)–C (8)–C (9) | 115.6 (6) |
| Br (03)–Mn (1)–Br (02) | 108.34 (3) | C (9)–C (8)–C (13) | 110.3 (6) |
| Br (04)–Mn (1)–Br (01) | 114.21 (4) | C (8)–C (13)–C (12) | 115.6 (8) |
| Br (04)–Mn (1)–Br (02) | 109.38 (4) | C (21)–C (22)–C (23) | 110.0 (6) |
| Br (04)–Mn (1)–Br (03) | 109.07 (4) | C (14)–C (15)–C (16) | 110.4 (6) |
| C (14)–N (1)–C (21) | 118.7 (4) | C (14)–C (19)–C (18) | 109.3 (6) |
| C (20)–N (1)–C (14) | 113.5 (4) | C (6)–C (1)–C (2) | 109.0 (7) |
| C (20)–N (1)–C (21) | 109.3 (4) | C (24)–C (25)–C (26) | 114.3 (6) |
| N (1)–C (14)–C (15) | 108.5 (4) | C (25)–C (24)–C (23) | 113.3 (6) |
| C (19)–C (14)–N (1) | 114.6 (4) | C (24)–C (23)–C (22) | 110.3 (7) |
| C (19)–C (14)–C (15) | 112.4 (5) | C (3)–C (2)–C (1) | 113.3 (7) |
| C (26)–C (21)–N (1) | 110.7 (4) | C (17)–C (16)–C (15) | 113.3 (8) |
| C (22)–C (21)–N (1) | 117.0 (4) | C (11)–C (10)–C (9) | 114.4 (8) |
| C (22)–C (21)–C (26) | 112.9 (5) | C (4)–C (5)–C (6) | 112.1 (9) |
| C (21)–C (26)–C (25) | 109.4 (5) | C (17)–C (18)–C (19) | 111.6 (7) |
| C (8)–N (2)–C (6) | 116.2 (5) | C (8)–C (9)–C (10) | 116.1 (7) |
| C (8)–N (2)–C (7) | 116.2 (7) | C (12)–C (11)–C (10) | 114.6 (10) |
| C (7)–N (2)–C (6) | 110.7 (5) | C (18)–C (17)–C (16) | 111.6 (6) |
| C (1)–C (6)–N (2) | 112.6 (6) | C (11)–C (12)–C (13) | 112.6 (8) |
| C (5)–C (6)–N (2) | 111.2 (6) | C (2)–C (3)–C (4) | 111.0 (7) |
| C (5)–C (6)–C (1) | 112.0 (6) | C (5)–C (4)–C (3) | 111.5 (10) |

Table S3. Main parameters of processing and refinement of (C₁₃H₁₄N)₂MnBr₄ and (C₁₃H₂₆N)₂MnBr₄.

| Compound | (C ₁₃ H ₁₄ N) ₂ MnBr ₄ | (C ₁₃ H ₂₆ N) ₂ MnBr ₄ |
|---------------------------|--|--|
| Sp.Gr. | P1 | P2 ₁ /c |
| <i>a</i> , Å | 8.51480(28) | 11.62635(35) |
| <i>b</i> , Å | 8.63446(29) | 30.76613(89) |
| <i>c</i> , Å | 10.66282(41) | 9.53011(32) |
| α , ° | 87.0893(22) | 90 |
| β , ° | 67.2425(19) | 104.9861(22) |
| γ , ° | 87.1786(24) | 90 |
| <i>V</i> , Å ³ | 721.603(45) | 3292.96(18) |
| <i>Z</i> | 4 | 4 |

| 2θ -interval, ° | 7-100 | 0-0 |
|------------------------|-------|------|
| R_{wp} , % | 3.33 | 3.35 |
| R_p , % | 2.58 | 2.52 |
| χ^2 | 1.81 | 1.94 |
| R_B , % | 1.94 | 2.43 |
