Variable Luminescence and Chromaticity of Homoleptic Frameworks of the Lanthanides together with Pyridylpyrazolates

Heba Youssef, Alexander E. Sedykh, Jonathan Becker, Thomas Schäfer, Ilya V. Taydakov, Huanrong R. Li, and Klaus Müller-Buschbaum*
Table of Contents

Crystallographic Data ............................................................................................................. 2
Interatomic Distances and Angles ........................................................................................... 4
Powder Diffraction .................................................................................................................. 7
Photophysical Properties ....................................................................................................... 12
Thermal Analysis .................................................................................................................... 31
IR Spectroscopy ..................................................................................................................... 32
Experimental Section ............................................................................................................ 37
## Crystallographic Data

CCDC 2075974 (1), 2075975 (2), 2075976 (3), 2075977 (4), 2075978 (5), 2075980 (7), 2075981 (8), 2075982 (9), and 2075983 (10) contain the supplementary crystallographic data. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

### Table S1. Crystallographic data of \( \frac{1}{2}[\text{Ln}(3\text{-PyPz})_3] \) (1-5).

| Compound | \( \frac{1}{2}[\text{Sm}(3\text{-PyPz})_3] \) | \( \frac{1}{2}[\text{Eu}(3\text{-PyPz})_3] \) | \( \frac{1}{2}[\text{Gd}(3\text{-PyPz})_3] \) | \( \frac{1}{2}[\text{Tb}(3\text{-PyPz})_3] \) | \( \frac{1}{2}[\text{Dy}(3\text{-PyPz})_3] \) |
|----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| CCDC number | 2075974                         | 2075975                         | 2075976                         | 2075977                         | 2075978                         |
| Empirical formula | \( \text{C}_{24} \text{H}_{16} \text{N}_{2} \text{Sm} \) | \( \text{C}_{24} \text{H}_{16} \text{N}_{2} \text{Eu} \) | \( \text{C}_{24} \text{H}_{16} \text{N}_{2} \text{Gd} \) | \( \text{C}_{24} \text{H}_{16} \text{N}_{2} \text{Tb} \) | \( \text{C}_{24} \text{H}_{16} \text{DyN}_{2} \) |
| \( M_\text{r} \)/g·mol\(^{-1} \) | 582.82                           | 584.43                           | 589.72                           | 591.39                           | 594.97                           |
| \( T \)/K | 100(2)                           | 100(2)                           | 100(2)                           | 200(2)                           | 100(2)                           |
| \( \lambda \)/pm | 71.073,                           | 71.073,                           | 71.073,                           | 71.073,                           | 71.073,                           |
| Crystal system | Cubic                           | Cubic                           | Cubic                           | Cubic                           | Cubic                           |
| Space group | \( \text{P}a\overline{3} \)          | \( \text{P}a\overline{3} \)          | \( \text{P}a\overline{3} \)          | \( \text{P}a\overline{3} \)          | Cubic                           |
| \( a, b, c \)/pm | 1711.0(2)                        | 1710.4(1)                        | 1702.4(1)                        | 1707.0(1)                        | 1699.9(1)                        |
| \( \alpha, \beta, \gamma \)/° | 90                               | 90                               | 90                               | 90                               | 90                               |
| \( V \)/10\(^6\)pm\(^3\) | 5009(2)                          | 50034(2)                         | 4934.3(4)                        | 4973.6(3)                        | 4912.6(4)                        |
| \( Z \) | 8                               | 8                               | 8                               | 8                               | 8                               |
| \( \rho_{\text{calc}} \)/g·cm\(^{-3} \) | 1.546                            | 1.552                            | 1.588                            | 1.580                            | 1.609                            |
| \( \mu \)/mm\(^{-1} \) | 2.374                           | 2.536                           | 2.718                           | 2.873                           | 3.072                            |
| \( F(000) \) | 2296                            | 2304                            | 2312                            | 2320                            | 2328                            |
| Crystal size / mm\(^{3} \) | 0.039 x 0.023 x 0.168 x 0.129 x | 0.047 x 0.043 x 0.047 x 0.054 x | 0.254 x 0.208 x 0.057 x 0.062 x | 0.079 x 0.062 x 0.079 x 0.082 x | 0.079 x 0.062 x 0.079 x 0.082 x |
| \( 2\theta_{\text{min}} \)/° | 2.062                            | 2.062                            | 2.072                            | 2.066                            | 2.396                            |
| \( 2\theta_{\text{max}} \)/° | 26.730                           | 27.502                           | 28.364                           | 30.604                           | 27.073                           |
| Reflections collected | 46979                           | 45916                           | 57689                           | 64936                           | 17575                           |
| Independent reflections | 1786                            | 1936                            | 2072                            | 2566                            | 1814                            |
| R(int) | 0.1383                            | 0.0591                            | 0.3466                            | 0.1016                            | 0.1026                            |
| Completeness to \( \theta = 25.242^\circ \) | 100.0 %                         | 100.0 %                         | 100.0 %                         | 99.9 %                          | 99.9 %                          |
| No. Of parameters | 103                           | 103                           | 103                           | 103                           | 103                           |
| GOF | 1.097                             | 1.139                             | 0.938                             | 1.060                             | 1.046                             |
| Final R indices \([I > 2\sigma(I)]\) | \( R_I = 0.0312, wR_2 \) = 0.0611 | \( R_I = 0.0216, wR_2 = 0.0457 \) | \( R_I = 0.0318, wR_2 = 0.0567 \) | \( R_I = 0.0297, wR_2 = 0.0527 \) | \( R_I = 0.0412, wR_2 = 0.0794 \) |
| R indices (all data) | \( R_I = 0.0535, wR_2 = 0.0483 \) | \( R_I = 0.0293, wR_2 = 0.0483 \) | \( R_I = 0.0727, wR_2 = 0.0644 \) | \( R_I = 0.0563, wR_2 = 0.0624 \) | \( R_I = 0.0755, wR_2 = 0.0921 \) |
| \( \Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} \)/e·10\(^{6}\)pm\(^{3} \) | 1.326, -0.662 | 0.388, -0.652 | 1.417, -0.510 | 0.510, -0.786 | 1.590, -1.101 |
### Table S2. Crystallographic data of $\frac{3}{2}[$Ln(4-PyPz)$_3$] (6-10).

| Compound | $\frac{3}{2}$[Sm(4-PyPz)$_3$] | $\frac{3}{2}$[Eu(4-PyPz)$_3$] | $\frac{3}{2}$[Gd(4-PyPz)$_3$] | $\frac{3}{2}$[Tb(4-PyPz)$_3$] | $\frac{3}{2}$[Dy(4-PyPz)$_3$] |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| CCDC number | 2075979 | 2075980 | 2075981 | 2075982 | 2075983 |
| Empirical formula | C$_{24}$H$_{18}$N$_5$Sm | C$_{24}$H$_{18}$N$_5$Eu | C$_{24}$H$_{18}$N$_5$Gd | C$_{24}$H$_{18}$N$_5$Tb | C$_{24}$H$_{18}$N$_5$Dy |
| M / g·mol$^{-1}$ | 582.82 | 584.43 | 589.72 | 591.39 | 594.97 |
| T / K | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| λ / pm | 71.073, 71.073 | 71.073, 71.073 | 71.073, 71.073 | 71.073, 71.073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P2$_1$/n | P2$_1$/n | P2$_1$/n | P2$_1$/n | P2$_1$/n |
| a / pm | 923.5(1) | 921.2(1) | 919.5(2) | 918.3(2) | 916.8(1) |
| b / pm | 1682.7(1) | 1681.4(1) | 1681.4(2) | 1679.1(3) | 1677.5(1) |
| c / pm | 1582.0(1) | 1577.9(1) | 1578.3(2) | 1576.6(3) | 1572.6(1) |
| α / ° | 90 | 90 | 90 | 90 | 90 |
| β / ° | 102.31(1) | 102.30(1) | 102.34(1) | 102.33(1) | 102.22(1) |
| γ / ° | 90 | 90 | 90 | 90 | 90 |
| V / 10$^6$ pm$^3$ | 2401.8(2) | 2387.8(2) | 2383.7(6) | 2375.0(6) | 2363.6(2) |
| Z | 4 | 4 | 4 | 4 | 4 |
| $\rho$calc / g·cm$^{-3}$ | 1.612 | 1.626 | 1.643 | 1.654 | 1.672 |
| $\mu$ / mm$^{-1}$ | 2.475 | 2.657 | 2.813 | 3.009 | 3.192 |
| F(000) | 1148 | 1152 | 1156 | 1160 | 1164 |
| Crystal size / mm$^3$ | 0.037 x 0.035 x 0.059 x 0.036 x 0.029 x 0.022 x 0.017 | 0.253 x 0.226 x 0.084 x 0.076 x | 0.253 x 0.226 x 0.084 x 0.076 x |
| 2θmax / ° | 1.789 | 1.792 | 2.368 | 2.645 | 1.797 |
| 2θmax / ° | 27.538 | 26.370 | 27.875 | 30.032 | 26.021 |
| Reflections collected | 77055 | 47406 | 87613 | 32018 | 98317 |
| Independent reflections | 5521 | 4891 | 5685 | 6925 | 4664 |
| $R$(int) | 0.0632 | 0.1014 | 0.1333 | 0.1191 | 0.0668 |
| Completeness to theta = 25.242° | 100.0 % | 100.0 % | 100.0 % | 99.9 % | 100.0 % |
| No. Of parameters | 307 | 307 | 307 | 308 | 307 |
| GOF | 1.045 | 1.056 | 1.086 | 1.024 | 1.084 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_I = 0.0209$, $R_I = 0.0329$, $R_I = 0.0343$, $R_I = 0.0476$, $R_I = 0.0182$, | $R_I = 0.0294$, $R_I = 0.0510$, $R_I = 0.0553$, $R_I = 0.0778$, $R_I = 0.0233$, | | |
| 2σ(I) | | | | |
| $R$ indices (all data) | $R_I = 0.0294$, $R_I = 0.0510$, $R_I = 0.0553$, $R_I = 0.0778$, $R_I = 0.0233$, | | | |
| | $wR_I = 0.0441$ | $wR_I = 0.0739$ | $wR_I = 0.0806$ | $wR_I = 0.1100$ | $wR_I = 0.0385$ |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ / e·pm$^{-3}$ | 1.284, -0.477 | 1.785, -1.072 | 1.747, -0.878 | 1.894, -1.774 | 1.130, -0.600 |
### Interatomic Distances and Angles

**Table S3.** Selected interatomic distances (pm) and angles (°) of \([\text{Ln}(3\text{-PyPz})_3](1-5)\). Symmetry operations: I - z+1,x+1/2,-y+3/2 II y-1/2,-z+3/2,-x+1 III x-1/2,y,-z+3/2 IV y-1/2,-x+3/2 V z-1/2,x,-y+3/2.

| Compound        | \(d_1[^{\text{Sm(3-PyPz)}}]\) | \(d_2[^{\text{Eu(3-PyPz)}}]\) | \(d_3[^{\text{Gd(3-PyPz)}}]\) | \(d_4[^{\text{Tb(3-PyPz)}}]\) | \(d_5[^{\text{Dy(3-PyPz)}}]\) |
|-----------------|------------------|------------------|------------------|------------------|------------------|
| Ln-N2           | 241.2(3)         | 239.9(2)         | 238.5(4)         | 237.4(2)         | 236.0(4)         |
| Ln-N3           | 245.9(3)         | 245.2(2)         | 243.6(4)         | 242.0(2)         | 241.0(4)         |
| Ln-N1\(\text{III}\) | 262.0(3)         | 261.3(2)         | 258.6(4)         | 259.3(2)         | 256.5(4)         |
| N2-Ln-N2\(\text{I}\) | 85.8(1)          | 85.6(1)          | 85.6(2)          | 85.8(1)          | 85.9(2)          |
| N2-Ln-N3        | 32.7(1)          | 32.8(1)          | 33.1(2)          | 33.1(1)          | 33.2(2)          |
| N2\(\text{II}\)-Ln-N3 | 82.8(1)          | 82.7(1)          | 82.6(2)          | 83.1(1)          | 83.0(2)          |
| N2\(\text{II}\)-Ln-N3 | 117.9(1)         | 117.8(1)         | 118.1(1)         | 118.4(1)         | 118.5(2)         |
| N3-Ln-N3\(\text{II}\) | 113.0(1)         | 113.0(1)         | 113.1(8)         | 113.5(1)         | 113.5(1)         |
| N2-Ln-N1\(\text{III}\) | 161.3(1)         | 161.2(1)         | 161.3(1)         | 161.7(1)         | 161.6(2)         |
| N2\(\text{II}\)-Ln-N1\(\text{III}\) | 109.6(1)        | 109.8(1)         | 109.7(1)         | 109.3(1)         | 109.3(2)         |
| N2\(\text{II}\)-Ln-N1\(\text{III}\) | 84.8(1)          | 84.9(1)          | 84.9(2)          | 85.1(1)          | 84.9(2)          |
| N3-Ln-N1\(\text{III}\) | 155.5(1)         | 155.4(1)         | 155.3(2)         | 154.8(1)         | 154.8(2)         |
| N3\(\text{III}\)-Ln-N1\(\text{III}\) | 80.6(1)          | 80.6(1)          | 80.7(2)          | 80.6(1)          | 80.6(2)          |
| N3\(\text{III}\)-Ln-N1\(\text{III}\) | 76.9(1)          | 77.0(1)          | 76.6(1)          | 76.2(1)          | 76.1(2)          |
| N1\(\text{III}\)-Ln-N1\(\text{IV}\) | 83.1(1)          | 83.0(1)          | 83.1(2)          | 83.0(1)          | 83.1(2)          |
Table S4. Selected interatomic distances (pm) and angles (°) of $\text{[Ln(4-PyPz)$_3$)$_2$}]$ (6-10). Symmetry operations: : I $x+1/2,-y+1/2,z+1/2$ II $-x+3/2,y-1/2,-z+3/2$ III $x+1,y,z$.

| Compound          | $d_{\text{Sm(4-PyPz)$_3$]]}}$ | $d_{\text{Eu(4-PyPz)$_3$]]}}$ | $d_{\text{Gd(4-PyPz)$_3$]]}}$ | $d_{\text{Tb(4-PyPz)$_3$]]}}$ | $d_{\text{Dy(4-PyPz)$_3$]]}}$ |
|-------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Ln-N2             | 242.0(2)                      | 240.8(4)                      | 240.7(4)                      | 238.8(4)                      | 237.5(2)                      |
| Ln-N5             | 242.5(2)                      | 241.0(4)                      | 240.4(4)                      | 239.1(4)                      | 237.8(2)                      |
| Ln-N8             | 242.7(2)                      | 241.4(4)                      | 240.6(4)                      | 239.1(4)                      | 238.0(2)                      |
| Ln-N9             | 247.6(2)                      | 246.2(4)                      | 245.5(4)                      | 244.4(4)                      | 242.9(2)                      |
| Ln-N6             | 248.4(2)                      | 247.6(4)                      | 246.3(4)                      | 245.6(5)                      | 243.4(2)                      |
| Ln-N3             | 250.4(2)                      | 248.6(4)                      | 247.8(4)                      | 246.8(4)                      | 245.3(2)                      |
| Ln-N1$ ^{1}$      | 258.9(2)                      | 257.7(4)                      | 256.5(4)                      | 256.3(4)                      | 253.3(2)                      |
| Ln-N4$ ^{2}$      | 260.6(2)                      | 258.8(4)                      | 258.3(4)                      | 255.8(4)                      | 255.7(2)                      |
| Ln-N7$ ^{3}$      | 260.6(2)                      | 258.8(3)                      | 257.6(4)                      | 256.7(5)                      | 255.0(2)                      |
| N2-Ln-N5          | 86.2(1)                       | 86.1(1)                       | 86.1(1)                       | 86.0(2)                       | 85.8(1)                       |
| N2-Ln-N8          | 90.1(1)                       | 90.1(1)                       | 90.0(1)                       | 90.1(2)                       | 90.0(1)                       |
| N5-Ln-N8          | 84.5(1)                       | 84.5(1)                       | 84.6(1)                       | 84.4(2)                       | 84.6(1)                       |
| N2-Ln-N9          | 84.9(1)                       | 85.1(1)                       | 85.1(1)                       | 85.0(2)                       | 84.8(1)                       |
| N5-Ln-N9          | 115.8(1)                      | 116.0(1)                      | 116.0(1)                      | 116.1(2)                      | 116.4(1)                      |
| N8-Ln-N9          | 32.2(1)                       | 32.4(1)                       | 32.2(1)                       | 32.7(2)                       | 32.8(1)                       |
| N2-Ln-N6          | 118.3(1)                      | 118.4(1)                      | 118.4(1)                      | 118.7(2)                      | 118.7(1)                      |
| N5-Ln-N6          | 32.0(1)                       | 32.3(1)                       | 32.3(1)                       | 32.7(2)                       | 32.8(1)                       |
| N8-Ln-N6          | 85.2(1)                       | 85.1(1)                       | 85.3(1)                       | 84.9(2)                       | 84.9(1)                       |
| N9-Ln-N6          | 115.6(1)                      | 115.7(1)                      | 115.6(1)                      | 115.6(2)                      | 115.8(1)                      |
| N2-Ln-N3          | 32.0(1)                       | 32.1(1)                       | 32.2(1)                       | 32.2(2)                       | 32.7(1)                       |
| N5-Ln-N3          | 82.8(1)                       | 82.6(1)                       | 82.7(1)                       | 82.8(2)                       | 82.5(1)                       |
| N8-Ln-N3          | 121.2(1)                      | 121.3(1)                      | 121.3(1)                      | 121.4(2)                      | 121.7(1)                      |
| N9-Ln-N3          | 115.2(1)                      | 115.3(1)                      | 115.4(1)                      | 115.2(2)                      | 115.4(1)                      |
| N6-Ln-N3          | 109.8(1)                      | 109.8(1)                      | 109.9(1)                      | 110.4(2)                      | 110.3(1)                      |
| N2-Ln-N1$ ^{1}$   | 115.3(1)                      | 115.4(1)                      | 115.2(1)                      | 115.0(2)                      | 115.3(1)                      |
| N5-Ln-N1$ ^{1}$   | 87.6(1)                       | 87.5(1)                       | 87.4(1)                       | 87.5(2)                       | 87.1(1)                       |
| N8-Ln-N1$ ^{1}$   | 152.9(1)                      | 152.7(1)                      | 153.0(1)                      | 153.0(2)                      | 152.7(1)                      |
| N9-Ln-N1$ ^{1}$   | 150.8(1)                      | 150.7(1)                      | 150.9(1)                      | 150.9(2)                      | 151.0(1)                      |
| N6-Ln-N1$ ^{1}$   | 74.6(1)                       | 74.5(1)                       | 74.5(1)                       | 74.6(2)                       | 74.3(1)                       |
| N3-Ln-N1$ ^{1}$   | 83.3(1)                       | 83.3(1)                       | 83.0(1)                       | 82.8(2)                       | 82.7(1)                       |
| N2-Ln-N4$ ^{2}$   | 155.3(1)                      | 80.8(1)                       | 80.8(1)                       | 155.2(2)                      | 155.3(2)                      |
| N5-Ln-N4$ ^{2}$   | 115.2(1)                      | 156.4(1)                      | 115.3(1)                      | 115.3(2)                      | 115.6(1)                      |
| N8-Ln-N4$ ^{2}$   | 80.4(1)                       | 114.8(1)                      | 80.4(1)                       | 80.4(2)                       | 80.2(1)                       |
| N9-Ln-N4$ ^{2}$   | 74.9(1)                       | 82.4(1)                       | 74.6(1)                       | 74.7(2)                       | 74.5(1)                       |
| N6-Ln-N4$ ^{2}$   | 83.8(1)                       | 153.4(1)                      | 83.8(1)                       | 83.4(2)                       | 83.5(1)                       |
| N3-Ln-N4$ ^{2}$   | 154.4(1)                      | 75.9(1)                       | 154.3(1)                      | 154.2(2)                      | 154.1(1)                      |
| N1$ ^{1}$-Ln-N4$ ^{2}$ | 79.5(1)                  | 80.6(1)                       | 79.9(1)                       | 80.0(2)                       | 80.1(1)                       |
| N2-Ln-N7$ ^{2}$   | 80.8(1)                       | 155.3(1)                      | 80.8(1)                       | 80.7(2)                       | 80.7(1)                       |
| N5-Ln-N7$ ^{2}$   | 156.6(1)                      | 115.3(1)                      | 156.3(1)                      | 156.0(2)                      | 155.7(1)                      |
| N8-Ln-N7$ ^{2}$   | 114.7(1)                      | 80.3(1)                       | 115.0(1)                      | 115.3(2)                      | 115.3(1)                      |
| N9-Ln-N7$ ^{2}$   | 82.5(1)                       | 74.6(1)                       | 82.7(1)                       | 82.7(2)                       | 82.5(1)                       |
| N6-Ln-N7$ ^{2}$   | 153.4(1)                      | 83.7(1)                       | 153.2(1)                      | 153.1(2)                      | 153.0(1)                      |
|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| N3-Ln-N7\textsuperscript{III} | 75.9(1) | 154.5(1) | 75.7(1) | 75.3(2) | 75.2(1) |
| N\textsuperscript{I}-Ln-N7\textsuperscript{III} | 80.5(1) | 79.6(1) | 80.5(1) | 80.3(2) | 80.6(1) |
| N\textsuperscript{II}-Ln-N7\textsuperscript{III} | 82.6(1) | 82.7(1) | 82.7(1) | 82.9(2) | 80.7(1) |
Powder Diffraction

Figure S1. Comparison between the simulated diffraction pattern from the SCXRD data (black) and the observed X-ray powder diffraction pattern (red) of $\frac{1}{3}$[Eu(3-PzPy)$_3$] (2).

Figure S2. Comparison between the simulated diffraction pattern from the SCXRD data (Black) and the observed X-ray powder diffraction pattern (Red) of $\frac{1}{3}$[Gd(3-PzPy)$_3$]:Tb (3).
Figure S3. Comparison between the simulated diffraction pattern from the SCXRD data (Black) and the observed X-ray powder diffraction pattern (Red) of $\frac{1}{2}[\text{Tb}(3\text{-PyPz})_3]$ (4).

Figure S4. Comparison between the simulated diffraction pattern from the SCXRD data (Black) and the observed X-ray powder diffraction pattern (Red) of $\frac{3}{2}[\text{Dy}(3\text{-PyPz})_3]$ (5).
Figure S5. Pawley refinement of $\frac{1}{3}[\text{Eu(4-PyPz)$_3$}]$ (7), showing the experimental data (black) together with the Pawley fit (red), the corresponding difference plot (blue) as well as the hkl position markers (green).

Figure S6. Pawley refinement of $\frac{1}{3}[\text{Gd(4-PyPz)$_3$}]:\text{Eu}$$^{3+}$,$\text{Tb}$$^{3+}$ (8), showing the experimental data (black) together with the Pawley fit (red), the corresponding difference plot (blue) as well as the hkl position markers (green).
Figure S7. Pawley refinement of $\frac{1}{2}[\text{Tb}(4\text{-PyPz})_3]$ (9), showing the experimental data (black) together with the Pawley fit (red), the corresponding difference plot (blue) as well as the hkl position markers (green).

Figure S8. Pawley refinement of $\frac{1}{2}[\text{Dy}(4\text{-PyPz})_3]$ (10), showing the experimental data (black) together with the Pawley fit (red), the corresponding difference plot (blue) as well as the hkl position markers (green).
Table S5. Pawley refinement details and results for \( [\text{Ln}(4-\text{PyPz})_3] \) (6-10).

| Compound  | \( [\text{Sm}(4-\text{PyPz})_3] \) | \( [\text{Eu}(4-\text{PyPz})_3] \) | \( [\text{Gd}(4-\text{PyPz})_3] \) | \( [\text{Tb}(4-\text{PyPz})_3] \) | \( [\text{Dy}(4-\text{PyPz})_3] \) |
|-----------|------------------|------------------|------------------|------------------|------------------|
| \( R_{wp} \) | 1.7401           | 1.9505           | 1.6597           | 1.9598           | 1.8547           |
| GOF       | 0.9884           | 1.1330           | 1.0618           | 1.0540           | 1.0465           |
| \( a / \text{pm} \) | 922.3(1)         | 921.2(1)         | 919.3(1)         | 916.7(1)         | 916.0(1)         |
| \( b / \text{pm} \) | 1685.5(1)        | 1683.5(1)        | 1683.0(1)        | 1679.4(1)        | 1679.6(1)        |
| \( c / \text{pm} \) | 1601.6(1)        | 1599.8(1)        | 1597.9(1)        | 1595.3(1)        | 1592.8(1)        |
| \( \alpha / ^\circ \) | 90               | 90               | 90               | 90               | 90               |
| \( \beta / ^\circ \) | 102.475(1)       | 102.455(2)       | 102.460(2)       | 102.476(1)       | 102.444(1)       |
| \( \gamma / ^\circ \) | 90               | 90               | 90               | 90               | 90               |
| \( V / 10^6 \text{pm}^3 \) | 2430.8(1)        | 2422.7(2)        | 2413.9(1)        | 2398.0(1)        | 2392.9(1)        |
Figure S9. Normalized excitation and emission spectra of 3-PyPzH at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S10. Normalized excitation and emission spectra of 4-PyPzH at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S11. Normalized excitation and emission spectra of $^{3}_{\infty}$[Sm(3-PyPz)$_3$] (1) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S12. Normalized excitation and emission spectra of $^{3}_{6}$[Eu(3-PyPz)$_3$] (2) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S13. Normalized excitation and emission spectra of $\text{3}_{\infty} \text{[Gd(3-PyPz)$_2$]} \cdot \text{Eu}^{3+}, \text{Tb}^{3+}$ (3) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S14. Normalized excitation and emission spectra of $\text{[Tb(3-PyPz)$_3$]}$ (4) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S15. Normalized excitation and emission spectra of \( [\text{Dy(3-PyPz)}_3] \) (5) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S16. Normalized excitation and emission spectra of $\frac{3}{2}\text{[Sm(4-PyPz)$_3$]}$ (6) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S17. Normalized excitation and emission spectra of $^3_{\infty}[\text{Eu(4-PyPz)$_3$}]$ (7) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S18. Normalized excitation and emission spectra of $\text{Gd(4-PyPz)_{3}}$:Eu$^{3+}$,Tb$^{3+}$ (8) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S19. Normalized excitation and emission spectra of \( \lambda_{\text{em}} = 544 \text{ nm} \) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S20. Normalized excitation and emission spectra of $^{3}$D$_{0}$[Dy(4-PyPz)$_3$] (10) at room temperature (top) and 77K (bottom). Wavelengths at which the spectra were recorded are reported in the legends.
Figure S21. Normalized emission spectra of $\frac{1}{2}[(\text{Gd}_{1-x}\text{Eu}_{x}\text{Tb}_{y})_3(3-\text{PyPz})_3]:\text{Eu}^{3+},\text{Tb}^{3+}$ (3a-3f) at room temperature (top) and 77K (bottom), $\lambda_{exc} = 323$ nm.
Figure S22. Normalized emission spectra of $\left[\text{Gd}_{1-x-y}\text{Eu}_x\text{Tb}_y(4-\text{PyPz})_3\right]\cdot\text{Eu}^{3+},\text{Tb}^{3+}$ (8a-8f) at room temperature (top) and 77K (bottom), $\lambda_{\text{exc}} = 321$ nm.
Figure S23. Normalized excitation spectra of $\text{Gd}_{1-x-y}\text{Eu}_x\text{Tb}_y(3-\text{PyPz})_3\text{Eu}^{3+},\text{Tb}^{3+}$ (3a-3f) and $\text{Gd}_{1-x-y}\text{Eu}_x\text{Tb}_y(4-\text{PyPz})_3\text{Eu}^{3+},\text{Tb}^{3+}$ (8a-8f) at room temperature (top) and 77K (bottom). $\lambda_{em} = 545$ nm (left) and 621 nm (right).
Figure S24. Normalized emission and excitation spectra of \( \text{Eu}_{0.95}\text{Tb}_{0.05}(3\text{-PyPz})_3 \) (2a) (excitation spectrum, left, \( \lambda_{\text{em}} = 621 \text{ nm} \)) (emission spectrum, red, top) and \( \text{Tb}_{0.95}\text{Eu}_{0.05}(3\text{-PyPz})_3 \) (4a) (excitation spectrum, right, \( \lambda_{\text{em}} = 545 \text{ nm} \)) (emission spectrum, green, top) at 77K. \( \lambda_{\text{exc}} = 317 \text{ nm} \).
Figure S25. Normalized excitation and emission spectra of \( \text{Eu}_{0.95}\text{Tb}_{0.05}(3\text{-PyPz})_3 \) (2a) (top) and \( \text{Tb}_{0.95}\text{Eu}_{0.05}(3\text{-PyPz})_3 \) (4a) (bottom) at RT. Wavelengths at which the spectra were recorded are reported in the legends.
Figure S26. Chromaticity coordinate diagram (CIE 1931) of the emission colors of the series $\text{Gd}_{1-x}\text{Eu}_x\text{Tb}_y(4\text{-PyPz})$:Eu$^{3+}$, Tb$^{3+}$ (8b-8f) (triangle, black), $\text{Eu}_{0.95}\text{Tb}_{0.05}(3\text{-PyPz})$:Eu$^{3+}$, Tb$^{3+}$ (2a) (square, blue) and $\text{Tb}_{0.95}\text{Eu}_{0.05}(3\text{-PyPz})$: Eu$^{3+}$, Tb$^{3+}$ (circles, blue) at 77K.

Table S7. Chromaticity coordinates (x,y) for 3, 3a-3f, 8, 8a-8f, 2a and 4a at 77 K.

| compound | CIE, x | CIE, y |
|----------|--------|--------|
| $\text{Gd}(3\text{-PyPz})$:Eu$^{3+}$, Tb$^{3+}$ | 0.23306 | 0.37899 |
| $\text{Eu}_{0.95}\text{Tb}_{0.05}(3\text{-PyPz})$:Eu$^{3+}$, Tb$^{3+}$ | 0.28554 | 0.28001 |
| 99 % Gd +1 % Eu | 0.28554 | 0.28001 |
| 99.5 % Gd +0.5 % Eu | 0.30005 | 0.37495 |
| 97 % Gd +1 % Tb + 2 % Eu | 0.42248 | 0.42079 |
| 95 % Eu + 5 % Tb | 0.6519 | 0.32552 |
| 95 % Tb + 5 % Eu | 0.36027 | 0.56591 |
Table S8. Photophysical data of $\gamma$[Gd$_{1-x}$Eu$_x$Tb$_y$(3-PyPz)$_3$]:Eu$^{3+}$,Tb$^{3+}$ (3a-3f), $\delta$[Gd$_{1-x}$Eu$_x$Tb$_y$(4-PyPz)$_3$]:Eu$^{3+}$,Tb$^{3+}$ (8a - 8f), $\gamma$[Eu$_{0.95}$Tb$_{0.05}$(3-PyPz)$_3$] (2a) and $\delta$[Tb$_{0.95}$Eu$_{0.05}$(3-PyPz)$_3$] (4a) in the solid-state at room temperature and 77K.

| compound | $\tau^a$/ms | $\lambda_{ex}/\lambda_{em}$/nm $^b$ | $\tau^d$/ms | $\lambda_{ex}/\lambda_{em}$/nm $^d$ |
|----------|--------------|---------------------------------|--------------|---------------------------------|
|            |              |                                 |              |                                 |
| 3a        | 0.516(2)     | 323/621                         | 0.601(2)     | 323/621                         |
| 3b        | 0.651(1)     | 323/621                         | 0.880(4)     | 317/621                         |
| 3c        | 0.721(1)     | 323/621                         | 0.867(3)     | 317/621                         |
| 3d        | 0.411(3)     | 323/621                         | 0.808(2)     | 317/621                         |
| 3e        | 0.416(8)     | 323/621                         | 0.950(7)     | 323/621                         |
| 3f        | 0.698(2)     | 323/621                         | 1.014(3)     | 323/621                         |
| 3g        | 0.661(1)     | 321/621                         | 0.802(2)     | 314/621                         |
| 3h        | 0.581(3)     | 321/621                         | 0.73(2)      | 314/621                         |
| 3i        | 0.658(4)     | 321/545                         | 0.82(1)      | 314/545                         |
| 3j        | 0.581(1)     | 321/545                         | 0.81(1)      | 314/545                         |
| 3k        | 0.721(2)     | 321/545                         | 0.939(6)     | 314/545                         |
| 3l        | 0.750(2)     | 321/545                         | 0.887(5)     | 314/545                         |
| 3m        | 0.518(5)     | 466/621                         | 0.751(3)     | 317/621                         |
| 3n        | 0.559(2)     | 323/621                         | 0.751(4)     | 317/545                         |

[a] Emission lifetimes determined at 298 K. [b] Excitation and emission wavelengths for emission lifetime at 298 K. [c] Emission lifetime determined at 77 K. [d] Excitation and emission wavelengths for emission lifetime at 77 K.
Figure S27. Simultaneous DTA-TG analysis of \( \frac{2}{3} [\text{Tb(3-PyPz)}_3] (4) \) representing the group of isostructural compounds (1-5). The measurement was performed in a constant argon flow of 50 ml-min\(^{-1}\) with a heating rate of 5 K-min\(^{-1}\) from room temperature to 1000 °C.
**IR Spectroscopy**

**Figure S28.** The infrared spectrum (ATR) of coordination polymer $\frac{1}{2}[\text{Sm}(3\text{-PyPz})_3]$ (1).

**Figure S29.** The infrared spectrum (ATR) of coordination polymer $\frac{1}{2}[\text{Eu}(3\text{-PyPz})_3]$ (2).
Figure S30. The infrared spectrum (ATR) of coordination polymer $\frac{1}{3}[\text{Gd(3-PyPz)}_3]:\text{Eu}^{3+},\text{Tb}^{3+}$ (3).

Figure S31. The infrared spectrum (ATR) of coordination polymer $\frac{1}{4}[\text{Tb(3-PyPz)}_3]$ (4).
Figure S32. The infrared spectrum (ATR) of coordination polymer $\frac{1}{3}[\text{Dy(3-PyPz)}_3]$ (5).

Figure S33. The infrared spectrum (ATR) of coordination polymer $\frac{1}{3}[\text{Sm(4-PyPz)}_3]$ (6).
Figure S34. The infrared spectrum (ATR) of coordination polymer $\frac{1}{2}[\text{Eu}(4\text{-PyPz})_3]_n$ (7).

Figure S35. The infrared spectrum (ATR) of coordination polymer $\frac{1}{2}[\text{Gd}(4\text{-PyPz})_3]:\text{Eu}^{3+},\text{Tb}^{3+}$ (8).
Figure S36. The infrared spectrum (ATR) of coordination polymer $\mathrm{\Sigma_2[Tb(4-PyPz)_3]}$ (9).

Figure S37. The infrared spectrum (ATR) of coordination polymer $\mathrm{\Sigma_2[Dy(4-PyPz)_3]}$ (10).
Experimental Section

CHN Analysis: Carbon, hydrogen, and nitrogen elemental analyses were executed using a Thermo Scientific Flash EA 1112. The polymers were placed in a tin crucible with no less than one mass equivalent to V₂O₅. Specimens were made ready and stored under inert conditions till the time of the measurements. Coordination polymers 6 - 10 were heated in advance under vacuum (p = 1.0×10⁻³ mbar) for further drying.

Single Crystal X-ray Diffraction (SCXRD): Single-crystal X-ray measurements of 3[Tb(3-PyPz)] (4), and 4[Tb(4-PyPz)] (9) were performed on a BRUKER AXS Smart Apex diffractometer with graphite monochromator (Mo-Kα radiation; λ = 71.073 pm) and a BRUKER CRYOFLEX low-temperature system. The single-crystal X-ray determinations of the other 3D-coordination polymers were carried out on a BRUKER AXS D8 Venture diffractometer equipped with a dual ΦS microfocus source, collimating Quazar multilayer mirror, a PHOTON100 detector, and an OXFORD CRYOSYSTEMS 700 low-temperature system. Data indexing for 3[Tb(3-PyPz)] (4) was done at 200 K conversely the data collection for all the other compounds mounted at 100 K as a result of the cracking behavior of the respective single-crystal upon cooling to 100 K. All structures were solved utilizing direct methods, refined with SQUEEZE. The average volume is found to be 132±6 electrons for (6 and 7), 3 for (8), 11 for (9), and 10 for (10) electrons per unit cell was also identified. Depictions of the crystal structures were generated using DIAMOND.[6] ToposPro program package was used to determine the Topology of the polymers.[8]

Powder X-ray Diffraction (PXRD): Specimens for powder diffraction were firstly ground in a mortar and filled into Lindemann glass capillaries with either 0.5 or 0.3 mm diameter under an inert gas atmosphere and then sealed. Diffraction data were collected on an STOE STADI P diffractometer with a focusing Ge(111) monochromator and a Dectris MYTHEN 1K strip detector in Debye-Scherrer geometry using CuKα radiation (λ =154.056 pm). Data collection was done using the STOE Powder Diffraction Software Package WinXPOW and Pawley fits on the data were performed using TOPAS Academic.[6] The peak shapes were described with the Thompson-Cox-Hastings pseudo-Voigt function, absorption was estimated by composition and the axial divergence was approximated using the simple axial model.

Vibrational Spectroscopy: MIR spectra were recorded from several milligrams of the compounds with an ALPHA FT-IR spectrometer from Bruker optics (ATR module) using OPUS software. Figures S26-S35 in the Supporting Information contain the IR spectra of the products.

Photoluminescence Spectroscopy: The excitation and emission spectra were recorded for ground solid samples after filling them in quartz capillaries under argon. The measurements were performed at room temperature as well as 77 K (latter using the liquid nitrogen-filled assembly FL-1013 of HORIBA) under vacuum (p = 1.0×10⁻³ mbar) with a HORIBA Jobin Yvon Spex Fluorolog 3 spectrometer equipped with a 450 W Xe short-arc lamp (USHIO), double-grated excitation, and emission monochromators, and a photomultiplier tube (R928P) using the FluoroEssence™ software. Excitation and emission spectra were corrected for the spectral response of the monochromators and the detector using spectral corrections provided by the constructor. Besides, a photodiode reference detector was used to correct the excitation spectra for the spectral distribution of the lamp intensity. When required, the collection of the data was performed using an edge filter. Emission spectra with gating were recorded using a xenon flashlamp with a pulse repetition rate of 41 ms.

Photoluminescence quantum yields were determined with the above-mentioned HORIBA Jobin Yvon Spex Fluorolog 3 spectrometer equipped with a HORIBA Quanta-4® Integrating Sphere. For the measurements, solid samples were filled into Starna Micro Cell cuvettes (18-F/ST/C/Q/10 (fluorescence with ST/C closed photon counting) upgrade, or picosecond pulsed laser diode. Emission decays were recorded using DataStation software. Photoluminescence overall decay process times were determined using the above-mentioned HORIBA Jobin Yvon Spex Fluorolog 3 spectrometer equipped with a dual lamp housing (FL-1040A), a UV xenon flashlamp (Exilits FX-1102), and a TCSPC (time-correlated single-photon counting) upgrade, or picosecond pulsed laser diode. Emission decays were recorded using DataStation software. Exponential tail fitting was used for the calculation of resulting intensity decay using Decay Analysis Software 6. The quality of the fit was confirmed by χ² values being below 1.2.

Thermal properties: were determined by simultaneous DTA/TG (NETZSCH STA 409-PC) coupled with a mass-spectrometer (NETZSCH QMS 403 Alétos) in a constant argon flow of 50 ml/min⁻¹ with a heating rate of 5 K/min from room temperature to 1000 °C for 3[Tb(3-PyPz)] (4), and 4[Tb(4-PyPz)] (9). DTA curve was baseline corrected after the measurement using Origin™ software.

Synthesis and Analytical Data

General Information: All syntheses with the participation of lanthanides were performed under argon or using vacuum line, gloveboxes (MBräun Labmaster SP, Innovative Technology PureLab), Schlenk tubes, and Duran® glass ampoules (outer ø 10 mm, wall thickness 1.5 mm). Pyridine, dichloromethane, and cyclohexane were purified by distillation and dried by standard procedures or used from the solvent purification system SPS-800 by MBraun (Garching, Germany). Durene was purchased from J&K Scientific GMBH then was sublimed under dynamic vacuum (p = 1.0×10⁻³ mbar) for further drying and purification process. The bulk materials were characterized by powder X-ray diffraction (PXRD) as well as CHN analysis.
Starting Materials: 3-(3-pyridyl)pyrazole / 3-(1H-pyrazol-3-yl)pyridine (3-PyPzH) and 3-(4-pyridyl)pyrazole / 4-(1H-pyrazol-3-yl)pyridine (4-PyPzH) were synthesized as reported in the literature. The method in detail is described in the supporting information. The lanthanide metals (gadolinium: 99.95%, Smart Element; rest: >99%, Chempur) were purchased and used as received, as well as Hg (> 99.9%, Alfa Aesar) used for activation.

Synthesis of (1H-pyrazol-3-yl)pyridines, the general method

A mixture of acetylpyridine (15g, 124 mmol) and DMF-DMA (30mL, 26.9g, 225 mmol) was stirred at 90 °C on an oil bath. MeOH was removed via a short Vigreux column (10 cm) connected to a descending condenser. The reaction was stopped once the distillation of MeOH ceased (7-8 h) and the mixture was cooled to room temperature overnight. Afterward, 30 mL of hexane was added and the resulting suspension was stirred for 30 min and subsequently filtered. The obtained solid was washed with 2 portions of hexane (each of 8 mL, 160 mmol) was added in one portion and the resulted mixture was refluxed for 6 h with gentle stirring and then cooled to a room temperature. Further separation of (E/Z) isomer or by 30 mL of a mixture of hexane/EtOAc (3:1 by volume) for 4 h in the air. M.p. 54 °C.

(E/Z)-3-(dimethylamino)-1-(pyridin-3-yl)prop-2-en-1-one. Brown solid, Yield was 19.4 g (88%).

(E/Z)-3-(dimethylamino)-1-(pyridin-4-yl)prop-2-en-1-one. Brown crystals, Yield was 17.1 g (78%).

To a stirred warm (40°C) solution of 19.3 g (110 mmol) of the corresponding enaminoketone in 150 mL of 96% ethanol N₂H₄·H₂O (100 %, 8 mL, 160 mmol) was added in one portion and the resulted mixture was refluxed for 6 h with gentle stirring and then cooled to a room temperature. Further separation of (1H-pyrazol-3-yl)pyridines was varied for different isomers.

3-(1H-pyrazol-3-yl)pyridine / 3-(3-pyridyl)pyrazole (3-PyPzH)

The cooled reaction mixture was evaporated to dryness under diminished pressure, the resulting solid was dissolved in 150 mL of CH₂Cl₂. The organic solution was washed with brine (30 mL), dried over MgSO₄ and evaporated to dryness. The resulted oil was dried at 45°C and 0.1 torr for 4 h until a solid crystalline mass was formed. The yield was 14.2 g (89%). The compound is hygroscopic and deliquescent in the air. M.p. 54-55 °C (lit. 56-58°C).

³H NMR (300 MHz, CDCl₃): δ = 10.39 (br, s, 1H), 9.08 (m, 1H), 8.61 (dd, J = 4.9 Hz, J = 1.1 Hz, 1H), 8.12 (d, J = 7.7 Hz, 1H), 7.68 (dd, J = 2.5 Hz, 1H), 7.34 (m, 1H), 6.70 (d, J = 2.4 Hz, 1H) ppm.

4-(1H-pyrazol-3-yl)pyridine / 3-(4-pyridyl)pyrazole (4-PyPzH)

The cooled reaction mixture was evaporated to dryness under diminished pressure. The resulting solid was dissolved in 500 mL of CHCl₃. The organic solution was washed by 20 mL of brine, dried over MgSO₄ and evaporated to dryness. The resulting solid was suspended in 20 mL of hexane, filtered and crystals were dried in air. The yield is 12.9 g (81%) of yellow solid. M.p. 155-157 °C (lit. 157-158°C).

³H NMR (300 MHz, CDCl₃): δ = 11.5-11.0 (br, s, 1H), 8.65 (dd, J = 4.7 Hz, J = 1.7 Hz, 2H), 7.75 (dd, J = 4.6 Hz, J = 1.7 Hz, 2H), 7.70 (d, J = 2.5 Hz, 1H), 6.71 (d, J = 2.5 Hz, 1H) ppm.
Synthesis of $\text{[Sm(3-PyPz)₃]}$ (1): Sm metal (0.09 mmol) and 3-PyPzH (C₈H₇N₃, 0.35 mmol) were mixed with pyridine (C₆H₅N, 0.3 mL). The reaction mixture was sealed in an evacuated Duran® glass ampoule under reduced pressure (p = 1.0×10⁻³ mbar). Before applying a vacuum to the ampoule as well as for sealing of the ampoule, the solvent was frozen using liquid nitrogen. The ampoule was heated to 200 °C in 24 h and maintained at this temperature for 72 h. Afterward, the reaction mixture was cooled to room temperature for 48 h. Excess Sm metal was not observed, and the excess ligand was removed by sublimation in a temperature gradient from 80 °C to RT. Suitable cubic single-crystals were selected for a single-crystal X-ray diffraction (SCXRD) measurement. C₃₂H₂₄N₈O₃Sm (582.82 g·mol⁻¹): C 49.14 (calcld. 49.46); H 3.13 (3.11); N 21.32 (21.63) %. Yield: 43 mg (85 %). FT-IR (ATR): ν = 3087 (w), 2167 (w), 1977 (w), 1597 (w), 1578 (m), 1509 (w), 1466 (m), 1455 (m), 1409 (m), 1361 (m), 1348 (m), 1250 (w), 1209 (m), 1187 (s), 1123 (w), 1100 (w), 1075 (m), 1042 (s), 964 (m), 930 (m), 859 (w), 819 (m), 780 (s), 717 (w), 702 (s), 657 (w), 673 (s), 509 (w), 465 (s) cm⁻¹.

Synthesis of $\text{[Eu(3-PyPz)₃]}$ (2): The preparation was done as described for (1) but freshly-filed Eu metal (0.08 mmol) was added to 3-PyPzH (C₈H₇N₃, 0.31 mmol) together in 0.1 mL pyridine. The reaction mixture was sealed in an evacuated Duran® glass ampoule under reduced pressure (p = 1.0×10⁻³ mbar). Before applying a vacuum to the ampoule as well as for sealing of the ampoule, the solvent was frozen using liquid nitrogen. The ampoule was heated to 200 °C in 1 h and maintained at this temperature for 96 h. Then, the ampoule was cooled to room temperature for 72 h. Colorless crystals were obtained while the solution became red, which could be an indication of a complex formation where pyridine being coordinated. Excess Eu metal was not observed. Suitable cubic single-crystals were selected for a SCXRD measurement. C₃₂H₂₄N₈O₃Eu (584.42 g·mol⁻¹): C 49.04 (calcld. 49.32); H 3.19 (3.10); N 21.30 (21.57) %. Yield: 43 mg (85 %). FT-IR (ATR): ν = 3087 (w), 2175 (w), 1598 (w), 1578 (w), 1509 (w), 1466 (w), 1453 (w), 1408 (w), 1361 (w), 1348 (w), 1249 (w), 1209 (m), 1187 (m), 1123 (w), 1076 (m), 1043 (s), 964 (m), 931 (m), 819 (w), 779 (s), 701 (s), 657 (w), 673 (s), 509 (w), 465 (s) cm⁻¹.

Synthesis of $\text{[Eu}_{3}\text{Sm}_{2}\text{Eu}_{3} (3b-3f)}$: Six ratios were synthesized with 1 % Eu (3a), 0.5 % Eu (3b), 1 % Tb with 3 % Eu (3c), 1 % Eu with 2 % Eu (3d), 1 % Eu with 1 % Eu (3e) and 1 % Tb (3f). The required amounts of the freshly filed metals (0.08 mmol) were mixed and ground in a mortar to acquire the best homogeneity. The reactions were carried out as described in 3 with the same heating conditions after adding 0.1 mL of pyridine.

Synthesis of $\text{[Eu}_{2}\text{Sm}_{2} (4a)}$: A ratio of 5 % Eu was ground together with freshly filed Tb to earn the top homogeneity. The reaction was performed as described in 4 by adding 0.1 mL pyridine.

Synthesis of $\text{[Tb}_{3}\text{PyPzH}_{3}\text{CuH}_{2}\text{PyPzH}_{2} (7)}$: The preparation was similar as described for (1) by freshly-filed Eu metal (0.11 mmol) and 3-PyPzH (C₈H₇N₃, 0.32 mmol) in 0.3 mL pyridine. The reaction mixture was sealed in an evacuated Duran® glass ampoule under reduced pressure (p = 1.0×10⁻³ mbar). Before applying a vacuum to the ampoule as well as for sealing of the ampoule, the solvent was frozen using liquid nitrogen. The oven was heated to 180 °C in 24 h. Afterward, the temperature was raised to 230 °C in 48 h. The temperature was held for 96 h and then lowered to 25 °C in another 48 h. For an excess of the ligand and the activating Hg, the reaction was complete, resulting in highly reflective colorless crystals.

Synthesis of $\text{[CuH}_{2}\text{PyPzH}_{2} (8)}$: A mixture of Sm metal (0.11 mmol) and 3-PyPzH (C₈H₇N₃, 0.42 mmol) in durene (C₈H₇N₃, 0.74 mmol). The ampoule was heated to 270 °C in 1 h then 290 °C in 2 h. The temperature was held for 24 h and then lowered to 25 °C in another 3 h. Colorless single crystal was separated. The durene was sublimed in a temperature gradient from 85 °C to RT under reduced pressure (p = 1×10⁻³ mbar). C₃₂H₂₄N₈O₃Cu (584.42 g·mol⁻¹): C 49.32 (calcld. 49.32); H 4.08 (3.10); N 22.50 (21.57) %. Yield: Eu, 40 mg (80 %). FT-IR (ATR): ν = 3096 (w), 1698 (w), 1609 (s), 1550 (w), 1527 (w), 1460 (m), 1447 (m),
Synthesis of $\text{[Gd}_{2}(\text{PyPz})_{3}]^{3+}$: The preparation follows the same procedure as compound (6) but mixture of Gd metal (0.10 mmol) and 4-PyPzH (CsH2N3, 0.37 mmol) in 0.3 mL and pyridine (CsH2N, 0.3 mL) was used. Highly reflective colorless single-crystals of the product was selected for a SCXRD measurement. Unknown low amounts of Eu and Tb were detected by PL-spectroscopy, which was not added to the reaction but is a result of low impurities accompanied with the metal source. C22H10N3Gd (589.71 g mol⁻¹): C 47.98 (calcd. 48.45); H 2.90 (3.05); N 20.69 (21.19) %. Yield: Gd, 62 mg (82 %).

Synthesis of $\text{[Tb}(\text{PyPz})_{3}]^{3+}$ (8): By mixing and grinding Gd metal in a mortar with 1 % Eu (8a), 0.5 % Eu (8b), 1 % Tb with 2 % Eu (8d), 1 % Tb with 1 % Eu (8c) and 1 % Tb (8f) to synthesize six co-doped samples differ in the Ln-content. 0.10 mmol of the mixture was taken in an Ampule where the reaction was carried out as described in 8 with the same heating conditions.

Synthesis of $\text{[Dy}(\text{PyPz})_{3}]^{3+}$ (9): A freshly filed Tb metal (0.08 mmol) and 4-PyPzH (CsH2N3, 0.29 mmol), in pyridine (CsH2N, 0.2 mL) together with a catalytic amount of Hg (0.1 mmol), were treated similar to compound (6). The oven was heated to 200 °C in 72 h and then lowered to 25 °C in another 72 h giving colorless single-crystals suitable for a SCXRD measurement. C22H10N3Tb (591.401 g mol⁻¹): C 49.72 (calcd. 49.74); H 1.17 (3.07); N 11.02 (13.62) %. Yield: 42.5 mg (85 %).

Synthesis of $\text{[Dy}(\text{PyPz})_{3}]^{3+}$ (10): The preparation is similar to compound 6, but Dy metal (0.10 mmol) and 4-PyPzH (CsH2N3, 0.38 mmol) were used giving colorless single-crystals. C22H10N3Dy (594.96 g mol⁻¹): C 47.63 (calcd. 48.45); H 2.90 (3.05); N 20.69 (21.19) %. Yield: Dy, 60.4 mg (96 %). FT-IR (ATR): ν = 3095 (w), 2169 (w), 1977 (w), 1699 (w), 1611 (s), 1550 (m), 1413 (s), 1268 (w), 1211 (s), 1076 (m), 1049 (m), 1008 (s), 971 (w), 930 (s), 845 (w), 832 (w), 771 (s), 761 (s), 740 (m), 697 (s), 653 (m), 529 (m), 462 (s) cm⁻¹.

References

[1] a) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv. 2015, 71, 3-8; b) G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3-8; c) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112-122.
[2] a) A. L. Spek, Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 9-18.
[3] a) A. L. Spek, Acta Crystallogr., Sect. D: Biol. Crystallogr. 2009, 65, 148-155; b) A. L. Spek, Inorg. Chim. Acta 2018, 470, 232-237; c) A. L. Spek, Acta Crystallogr. Sect. E: Crystallogr. Commun. 2020, 76, 1-11; d) A. Spek, J. Appl. Crystallogr. 2003, 36, 7-11.
[4] W. T. Pennington, J. Appl. Crystallogr. 1999, 32, 1029-1029.
[5] V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, Cryst. Growth Des. 2014, 14, 3576-3586.
[6] A. A. Coelho, J. Appl. Crystallogr. 2018, 51, 210-218.
[7] M. S. Wrighton, D. S. Ginley, D. L. Morse, J. Phys. Chem. 1974, 78, 2229-2233.
[8] a) M. R. Di Giudice, C. Mustazza, A. Borioni, F. Gatta, K. Tayebati, F. Amenta, P. Tucci, S. Pieretti, Arch. Pharm. Pharm. Med. Chem. 2003, 336, 143-154; b) V. J. Bauer, H. P. Dalalain, W. J. Fanshawe, S. Safir, E. Tocci, C. Boshart, J. Med. Chem. 1998, 41, 981-984.