

Electronic Supplementary Information

The increase of europium-based OLED luminance through reducing the excited state lifetime by mixed-ligand complex formation

Makarii I. Kozlov^a, Andrey A. Vashchenko^b, Alexander A. Pavlov^c, Alexander S. Goloveshkin^c, Egor V. Latipov^a, Natalia P. Kuzmina,^a and Valentina V. Utochnikova^{a*}

^a M.V. Lomonosov Moscow State University, 1/3 Leninskie Gory, Moscow, 119991, Russia

^b P.N. Lebedev Physical Institute, Leninsky prosp. 53, Moscow, 119992, Russia

^c A.N. Nesmeyanov Institute of Organoelement Compounds, Vavilova St. 28, Moscow, 119334, Russia

†Corresponding author:

E-mail: valentina.utochnikova@gmail.com

Powder X-ray diffraction data

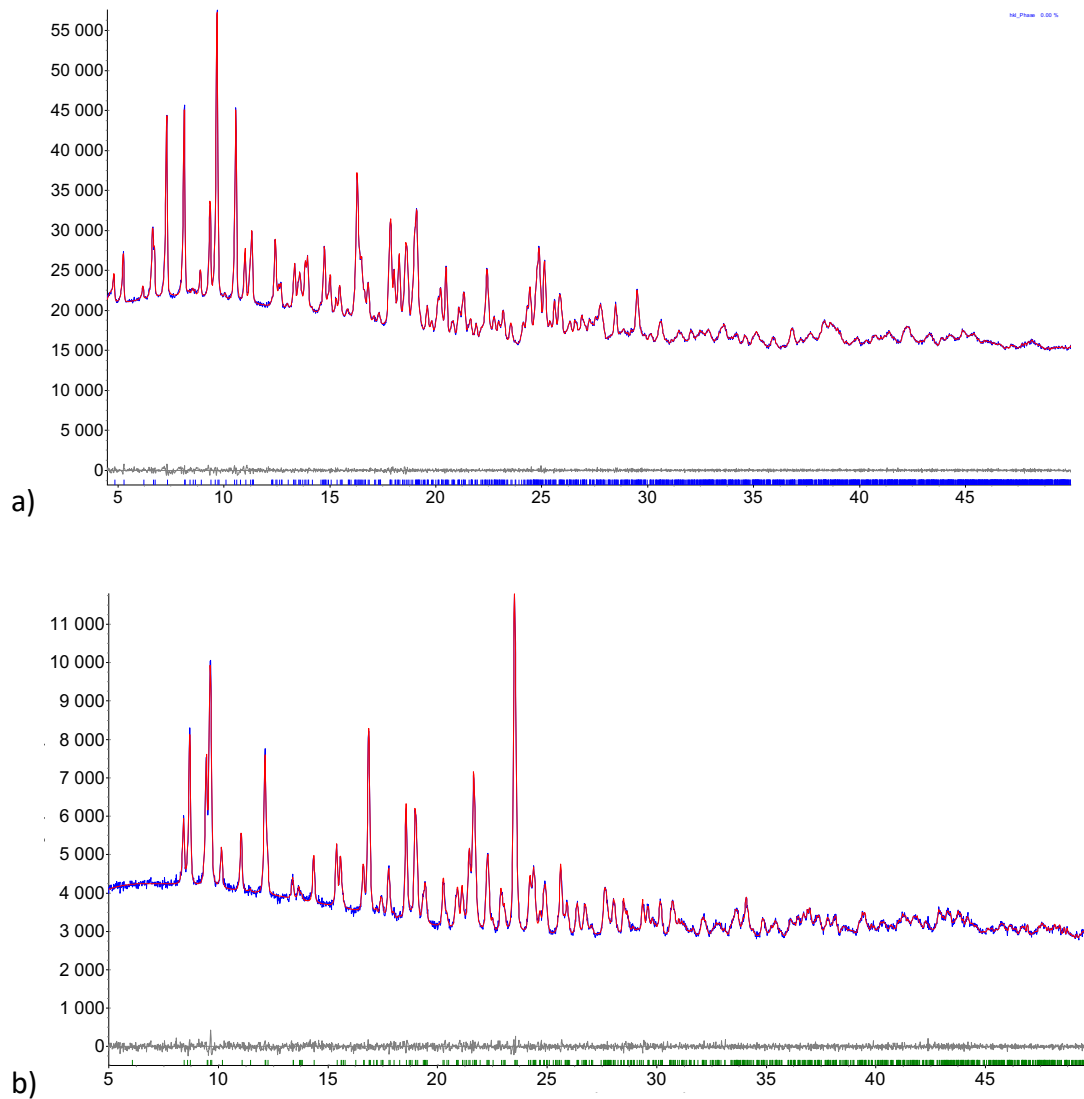


Figure S1. PXRD patterns of individual complexes a) $\text{Eu}(\text{dbm})_3\text{DPPZ}$ and b) $\text{Eu}(\text{tta})_3\text{DPPZ}$.

| | Eu(dbm) ₃ DPPZ | Eu(tta) ₃ DPPZ |
|-------------------|---------------------------|---------------------------|
| Space group | P21/c | P21/n |
| a, Å | 24.224(3) | 10.7364(12) |
| b, Å | 33.348(4) | 20.2453(16) |
| c, Å | 22.019(3) | 21.381(2) |
| β, ° | 144.115(5) | 102.038(8) |
| V, Å ³ | 10426(2) | 4545.2(8) |

The position, intensities and Miller indexes of the most intense peaks for Eu(dbm)₃DPPZ

| h | k | l | d | Th2 | I |
|---|----|----|----------|----------|------|
| 0 | 1 | 1 | 12.03762 | 7.33783 | 64.3 |
| 1 | 2 | 0 | 10.81147 | 8.17137 | 74.4 |
| 1 | 0 | 2 | 9.41249 | 9.38842 | 43.9 |
| 2 | 2 | 2 | 9.0982 | 9.71351 | 127 |
| 0 | 4 | 0 | 8.33742 | 10.60229 | 102 |
| 3 | 0 | 2 | 8.00681 | 11.0414 | 29.2 |
| 1 | 4 | 1 | 7.78335 | 11.35942 | 31 |
| 2 | 0 | 0 | 7.10043 | 12.45611 | 36.7 |
| 2 | 4 | 2 | 6.61251 | 13.37926 | 29.1 |
| 3 | 3 | 2 | 6.497 | 13.61825 | 23.2 |
| 1 | 5 | 1 | 6.3759 | 13.87817 | 28.6 |
| 3 | 1 | 1 | 6.32321 | 13.99439 | 32.9 |
| 1 | -3 | -1 | 5.98765 | 14.78292 | 41.3 |
| 2 | 3 | 3 | 5.88166 | 15.05084 | 32.1 |
| 2 | 5 | 1 | 5.7133 | 15.49704 | 23.5 |
| 4 | 0 | 4 | 5.42833 | 16.31601 | 113 |
| 1 | -4 | -1 | 5.40846 | 16.37634 | 24.3 |
| 1 | 6 | 1 | 5.38465 | 16.44925 | 25.9 |
| 4 | 1 | 4 | 5.35781 | 16.53223 | 44.5 |
| 4 | 2 | 2 | 5.25395 | 16.86142 | 25 |
| 2 | 6 | 1 | 4.96746 | 17.84158 | 54.2 |
| 2 | 6 | 2 | 4.94756 | 17.91392 | 91.9 |

| | | | | | |
|---|----|----|---------|----------|------|
| 3 | 5 | 3 | 4.90483 | 18.07128 | 55.4 |
| 3 | 3 | 4 | 4.84069 | 18.3128 | 75.1 |
| 1 | 6 | 2 | 4.78608 | 18.52355 | 21.3 |
| 5 | 1 | 4 | 4.7616 | 18.61962 | 73.2 |
| 2 | -1 | -1 | 4.74497 | 18.68549 | 35.8 |
| 3 | 0 | 0 | 4.73362 | 18.73068 | 31.7 |
| 3 | 1 | 0 | 4.68665 | 18.92014 | 25.3 |
| 2 | 1 | 4 | 4.66007 | 19.02902 | 64.2 |
| 1 | 7 | 1 | 4.65354 | 19.056 | 27.9 |
| 0 | 5 | 2 | 4.63809 | 19.12005 | 32.6 |
| 3 | 5 | 1 | 4.63293 | 19.14154 | 39.7 |
| 1 | 0 | -2 | 4.63012 | 19.15327 | 51.4 |
| 1 | 7 | 0 | 4.51682 | 19.63841 | 30.4 |
| 2 | -3 | -1 | 4.4019 | 20.15641 | 34.3 |
| 1 | -6 | -1 | 4.3782 | 20.26669 | 44.7 |
| 4 | 1 | 5 | 4.32359 | 20.52542 | 83.5 |
| 5 | 2 | 5 | 4.20248 | 21.1236 | 32.7 |
| 0 | 8 | 0 | 4.16871 | 21.29672 | 21.8 |
| 2 | -4 | -1 | 4.15578 | 21.36376 | 29.6 |
| 4 | 3 | 1 | 4.14959 | 21.396 | 26.9 |
| 1 | -7 | -1 | 3.95726 | 22.44905 | 46.7 |
| 2 | 7 | 0 | 3.95619 | 22.45519 | 50.2 |
| 4 | 4 | 1 | 3.9415 | 22.53998 | 25.4 |
| 3 | 7 | 1 | 3.83009 | 23.20465 | 32.7 |
| 0 | 4 | 3 | 3.82349 | 23.24524 | 22.7 |
| 6 | 3 | 4 | 3.7666 | 23.60137 | 22.5 |
| 1 | 3 | 4 | 3.68295 | 24.14537 | 23.3 |
| 1 | 9 | 1 | 3.65271 | 24.34832 | 38.5 |
| 5 | 1 | 6 | 3.6334 | 24.47973 | 86 |
| 1 | 9 | 0 | 3.58547 | 24.81217 | 35 |
| 4 | 7 | 4 | 3.58073 | 24.84554 | 37.8 |
| 5 | 2 | 6 | 3.57039 | 24.91865 | 118 |
| 6 | 2 | 6 | 3.53656 | 25.1609 | 123 |
| 1 | 4 | 4 | 3.53514 | 25.17112 | 22.8 |
| 3 | 8 | 1 | 3.49952 | 25.43163 | 27.9 |
| 5 | 3 | 6 | 3.47228 | 25.63453 | 58.5 |
| 6 | 3 | 6 | 3.44114 | 25.87052 | 46.5 |
| 0 | 10 | 0 | 3.33497 | 26.7091 | 22.4 |
| 4 | 8 | 4 | 3.30626 | 26.94539 | 21 |
| 6 | 6 | 4 | 3.2485 | 27.43375 | 22 |
| 6 | 6 | 5 | 3.23183 | 27.578 | 47.5 |

| | | | | | |
|---|-----|----|---------|----------|------|
| 5 | 5 | 6 | 3.2054 | 27.80996 | 33 |
| 1 | 6 | 4 | 3.19438 | 27.90784 | 25.8 |
| 6 | 1 | 7 | 3.12738 | 28.51826 | 87.5 |
| 6 | 2 | 7 | 3.08693 | 28.90006 | 20.2 |
| 6 | 7 | 4 | 3.06497 | 29.11167 | 20.5 |
| 6 | 3 | 7 | 3.02286 | 29.52637 | 61.4 |
| 3 | -6 | -1 | 3.02174 | 29.53751 | 31.1 |
| 5 | 1 | 7 | 3.02094 | 29.54551 | 40.2 |
| 1 | 11 | 0 | 2.96497 | 30.11634 | 24.3 |
| 8 | 1 | 7 | 2.91937 | 30.59813 | 20.1 |
| 2 | 9 | 4 | 2.91139 | 30.68414 | 20.1 |
| 5 | 6 | 1 | 2.90939 | 30.70576 | 24.8 |
| 1 | -11 | -1 | 2.78863 | 32.07049 | 25.1 |
| 2 | 11 | 0 | 2.78825 | 32.07491 | 20.6 |
| 7 | 0 | 8 | 2.75155 | 32.51455 | 24.8 |
| 8 | 2 | 8 | 2.67891 | 33.4217 | 25.5 |
| 6 | 2 | 8 | 2.65435 | 33.74013 | 22.4 |
| 2 | 13 | 2 | 2.49661 | 35.94228 | 24.2 |
| 6 | 0 | 0 | 2.36681 | 37.98669 | 21.2 |
| 7 | 3 | 9 | 2.35486 | 38.18691 | 37.3 |
| 4 | 13 | 2 | 2.32759 | 38.65198 | 20.1 |
| 2 | 14 | 2 | 2.32677 | 38.66615 | 31.6 |
| 5 | 6 | 8 | 2.31325 | 38.90116 | 24.6 |
| 2 | -11 | -2 | 2.30636 | 39.02211 | 40.2 |
| 8 | 9 | 7 | 2.29862 | 39.15881 | 44.5 |

The position, intensities and Miller indexes of the most intense peaks for Eu(tta)₃DPPZ

| h | k | l | m | d | Th2 | I |
|---|----|----|---|----------|----------|------|
| 0 | 2 | 0 | 2 | 10.12375 | 8.7275 | 23.3 |
| 1 | 1 | 0 | 4 | 9.32145 | 9.48033 | 19.5 |
| 1 | -1 | -1 | 4 | 9.16888 | 9.63846 | 24.9 |
| 0 | 2 | 1 | 4 | 9.1123 | 9.69845 | 24.4 |
| 1 | 1 | 1 | 4 | 7.9821 | 11.07569 | 11.3 |
| 0 | 2 | 2 | 4 | 7.27354 | 12.15852 | 26.3 |
| 1 | -1 | -3 | 4 | 6.15632 | 14.37573 | 12.5 |
| 0 | 2 | 3 | 4 | 5.7417 | 15.41994 | 17.8 |
| 1 | 3 | 0 | 4 | 5.67752 | 15.59532 | 13.5 |
| 2 | 0 | 0 | 2 | 5.25019 | 16.87356 | 34.7 |
| 1 | -3 | -2 | 4 | 5.24374 | 16.89447 | 23.1 |

| | | | | | | |
|---|----|----|---|---------|----------|------|
| 2 | -1 | -2 | 4 | 4.98367 | 17.78308 | 13.2 |
| 1 | 3 | 2 | 4 | 4.76905 | 18.5903 | 43.2 |
| 1 | -3 | -3 | 4 | 4.66765 | 18.99786 | 31.2 |
| 0 | 2 | 4 | 4 | 4.64553 | 19.08913 | 17.8 |
| 0 | 4 | 2 | 4 | 4.55615 | 19.46725 | 11.3 |
| 1 | 4 | 1 | 4 | 4.37336 | 20.28931 | 19.9 |
| 1 | 1 | 4 | 4 | 4.23755 | 20.9468 | 14.5 |
| 2 | -3 | -1 | 4 | 4.19894 | 21.14162 | 16.6 |
| 2 | 3 | 0 | 4 | 4.144 | 21.42519 | 11.8 |
| 0 | 3 | 4 | 4 | 4.13331 | 21.48125 | 25.9 |
| 1 | -1 | -5 | 4 | 4.11119 | 21.59823 | 12 |
| 0 | 1 | 5 | 4 | 4.09631 | 21.67763 | 18.9 |
| 0 | 4 | 3 | 4 | 4.09601 | 21.67924 | 47.4 |
| 2 | -1 | -4 | 4 | 4.07917 | 21.76983 | 15.6 |
| 2 | 2 | 2 | 4 | 3.99105 | 22.25658 | 14.7 |
| 0 | 5 | 1 | 4 | 3.97566 | 22.34383 | 20.8 |
| 1 | -2 | -5 | 4 | 3.87834 | 22.91203 | 19.7 |
| 1 | 5 | 0 | 4 | 3.77827 | 23.52741 | 26.8 |
| 0 | 5 | 2 | 4 | 3.77624 | 23.54025 | 154 |
| 2 | 1 | 3 | 4 | 3.76104 | 23.63674 | 19.4 |
| 1 | 5 | 1 | 4 | 3.67019 | 24.23057 | 12.9 |
| 1 | 4 | 3 | 4 | 3.66682 | 24.25323 | 15.8 |
| 1 | 3 | 4 | 4 | 3.64655 | 24.39009 | 10.4 |
| 2 | 4 | 0 | 4 | 3.64404 | 24.40712 | 20 |
| 1 | 0 | 5 | 2 | 3.63393 | 24.47607 | 10.4 |
| 3 | 0 | -1 | 2 | 3.5757 | 24.88101 | 14.9 |
| 1 | -3 | -5 | 4 | 3.56509 | 24.95626 | 17.4 |
| 1 | 5 | 2 | 4 | 3.47113 | 25.64313 | 40.4 |
| 0 | 6 | 1 | 4 | 3.33149 | 26.73746 | 14.2 |
| 0 | 4 | 5 | 4 | 3.22439 | 27.64292 | 15.3 |
| 1 | -5 | -4 | 4 | 3.17771 | 28.05722 | 15.4 |
| 1 | -6 | -2 | 4 | 3.12763 | 28.51592 | 25.1 |
| 2 | 5 | 1 | 4 | 3.11066 | 28.67481 | 14.5 |
| 0 | 6 | 3 | 4 | 3.03743 | 29.3815 | 26 |
| 2 | 3 | 4 | 4 | 3.01495 | 29.60561 | 10.5 |
| 3 | 3 | 1 | 4 | 2.99387 | 29.81881 | 10.7 |
| 1 | 5 | 4 | 4 | 2.95875 | 30.1812 | 15.5 |
| 0 | 5 | 5 | 4 | 2.90942 | 30.70543 | 12.7 |
| 2 | -5 | -4 | 4 | 2.90326 | 30.7722 | 11.3 |
| 3 | 4 | 0 | 4 | 2.87891 | 31.03896 | 12.2 |
| 0 | 7 | 3 | 4 | 2.67166 | 33.51502 | 11.7 |

| | | | | | | |
|---|----|----|---|---------|----------|------|
| 1 | 4 | 6 | 4 | 2.65557 | 33.72419 | 12.9 |
| 2 | 1 | 6 | 4 | 2.63685 | 33.97082 | 12.4 |
| 0 | 6 | 5 | 4 | 2.62641 | 34.11004 | 37 |
| 3 | 0 | 5 | 2 | 2.44497 | 36.72818 | 15.8 |
| 1 | -5 | -7 | 4 | 2.43413 | 36.89766 | 16.3 |
| 0 | 6 | 6 | 4 | 2.42451 | 37.04928 | 16.3 |
| 4 | 1 | 2 | 4 | 2.41193 | 37.24973 | 14.1 |
| 2 | 7 | 2 | 4 | 2.40739 | 37.32253 | 11.1 |
| 2 | 1 | 7 | 4 | 2.3746 | 37.85728 | 12.6 |
| 1 | 2 | 8 | 4 | 2.35475 | 38.18871 | 12 |
| 4 | -4 | -4 | 4 | 2.29222 | 39.27268 | 15.8 |
| 4 | -2 | -6 | 4 | 2.28471 | 39.40715 | 21.4 |
| 3 | -4 | -7 | 4 | 2.27755 | 39.53605 | 10.9 |
| 1 | -6 | -7 | 4 | 2.26103 | 39.83723 | 15.4 |

TGA data and IR-spectroscopy

The TGA data of individual complexes ($\text{Eu}(\text{dbm})_3\text{DPPZ}$ and $\text{Eu}(\text{tta})_3\text{DPPZ}\cdot\text{EtOH}$) and mixed-ligand complex $\text{Eu}(\text{dbm}+\text{tta})_3\text{DPPZ}$ (Fig. S2 a) correspond to typical decomposition of β -diketonate with phenanthroline derivatives. In the first stage of decomposition of $\text{Eu}(\text{tta})_3\text{DPPZ}\cdot\text{EtOH}$, in the range of 120–130°C molecule of EtOH is eliminated, which showed the presence of coordinated molecule.

In the spectra of $\text{Eu}(\text{dbm})_3\text{DPPZ}$, $\text{Eu}(\text{tta})_3\text{DPPZ}\cdot\text{EtOH}$, and $\text{Eu}(\text{dbm}+\text{tta})_3\text{DPPZ}$ (Fig. S2 b) low intensity bands at 3100–2800 cm^{-1} are observed, corresponding to the aromatic C–H vibrations of DPPZ and anionic ligands, bands at 1600–1500 cm^{-1} and 700–600 cm^{-1} , corresponding to C=O vibrations of β -diketonate.

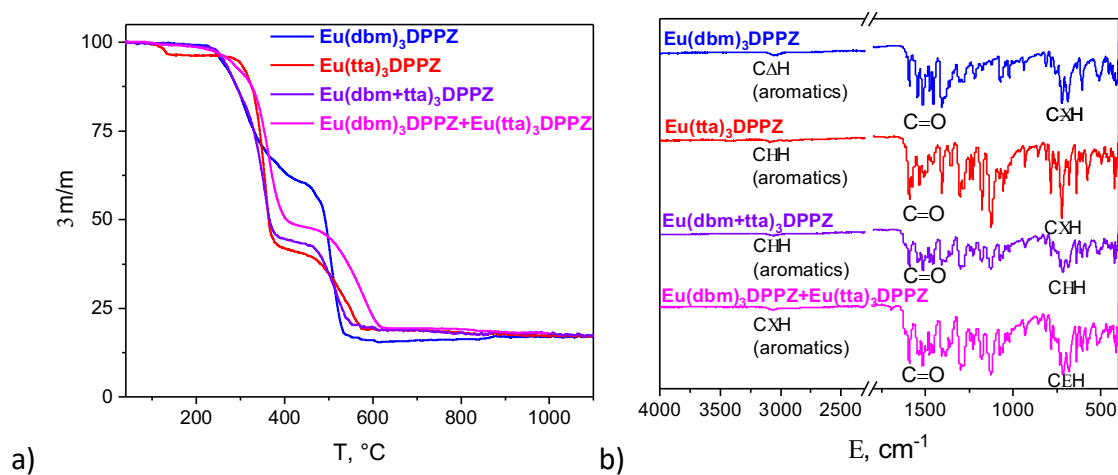


Figure S2. a) TGA curve of individual complexes ($\text{Eu}(\text{dbm})_3\text{DPPZ}$ and $\text{Eu}(\text{tta})_3\text{DPPZ}\cdot\text{EtOH}$) and mixed-ligand complex $\text{Eu}(\text{dbm}+\text{tta})_3\text{DPPZ}$. b) IR-spectrum of individual complexes ($\text{Eu}(\text{dbm})_3\text{DPPZ}$ and $\text{Eu}(\text{tta})_3\text{DPPZ}\cdot\text{EtOH}$) and mixed-ligand complexes $\text{Eu}(\text{dbm}+\text{tta})_3\text{DPPZ}$ and [$\text{Eu}(\text{dbm})_3\text{DPPZ} + \text{Eu}(\text{tta})_3\text{DPPZ}$].

NMR spectroscopy

^1H and ^{19}F NMR spectroscopy were also measured in DMSO-d_6 solvent.

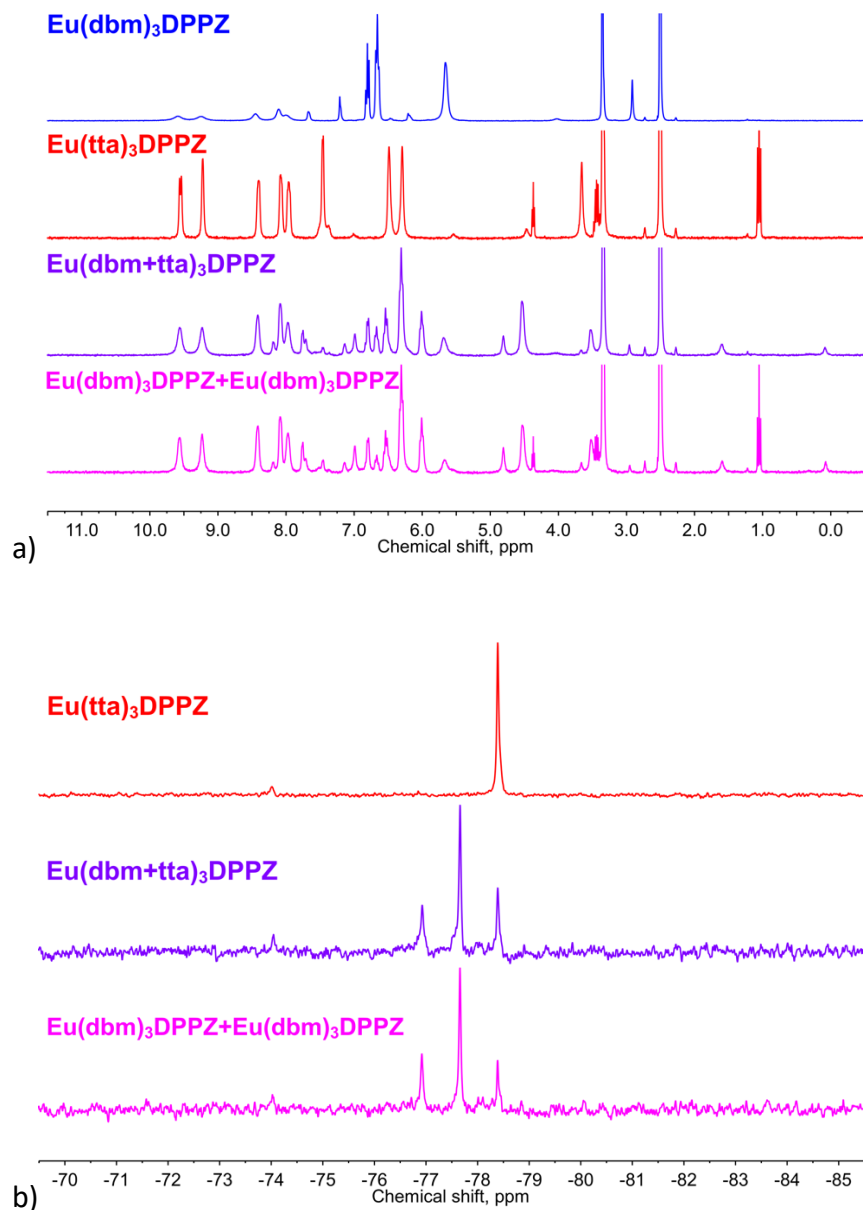


Figure S3. a) ^1H NMR spectra of individual complexes $\text{Eu}(\text{dbm})_3\text{DPPZ}$ and $\text{Eu}(\text{tta})_3\text{DPPZ}$ and mixed-ligand complexes $\text{Eu}(\text{dbm}+\text{tta})_3\text{DPPZ}$ and $[\text{Eu}(\text{dbm})_3\text{DPPZ} + \text{Eu}(\text{tta})_3\text{DPPZ}]$. b) ^{19}F NMR spectra of individual complex $\text{Eu}(\text{tta})_3\text{DPPZ}$ and mixed-ligand complex $\text{Eu}(\text{dbm}+\text{tta})_3\text{DPPZ}$ (DMSO-d_6).