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# Enhanced luminescence for detection of small molecules based on doped lanthanide compounds with dinuclear double-stranded helicate structure

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**Synthesis of doped compounds**

**$[(Sm_xGd_{1-x})_2L_2(DBM)_4(OAc)_2]$** IR (KBr, $cm^{-1}$): 3057 (w), 2844 (s), 2774 (w), 2601(w), 1733 (vs), 1690 (vs), 1555 (s), 1396 (vs), 1310 (s), 1207 (vs), 1155 (m), 1059 (m), 935 (vs), 864(w), 719 (m), 673 (w), 592 (m). UV−vis [MeOH, λ]: 210, 252, 352 nm.

**$[(Eu_xGd_{1-x})_2L_2(DBM)_4(OAc)_2]$** IR (KBr, $cm^{-1}$): 3061 (w), 2844 (s), 2772 (w), 2600(w), 1736 (vs), 1688 (vs), 1554 (s), 1396 (vs), 1310 (s), 1213 (vs), 1152 (m), 1058 (m), 938 (vs), 864(w), 717 (m), 672 (w), 592 (m). UV−vis [MeOH, λ]: 210, 252, 352 nm.

**$[(Yb_xGd_{1-x})_2L_2(DBM)_4(OAc)_2]$** IR (KBr, $cm^{-1}$): 3058 (w), 2846 (s), 2770 (w), 2598(w), 1734 (vs), 1690 (vs), 1554 (s), 1392 (vs), 1312 (s), 1215 (vs), 1154 (m), 1060 (m), 941 (vs), 864(w), 714 (m), 673 (w), 590 (m). UV−vis [MeOH, λ]: 210, 252, 352 nm.

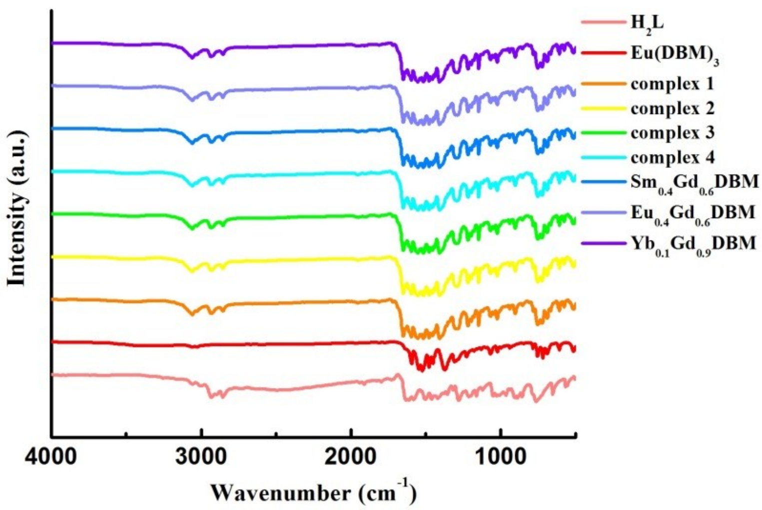



**Fig.S1** IR spectra of $H_2L$, $Eu(DBM)_3$, complexes **1-4** and $Ln_xGd_{1-x}DBM$.

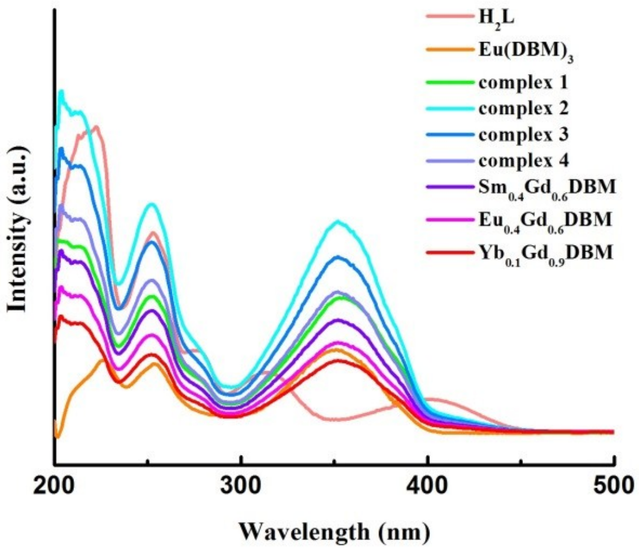



**Fig.S2** UV-vis absorption spectra of $H_2L$, $Eu(DBM)_3$, complexes **1-4** and $Ln_xGd_{1-x}DBM$.

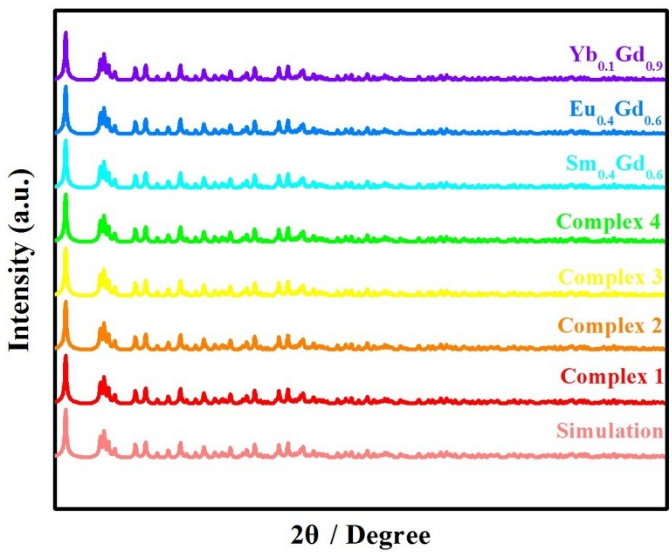



**Fig.S3** PXRD patterns for simulation, complexes **1-4** and $Ln_xGd_{1-x}DBM$.

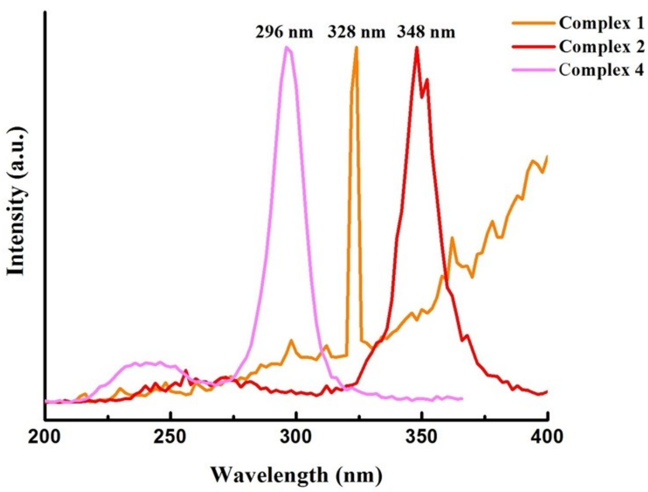
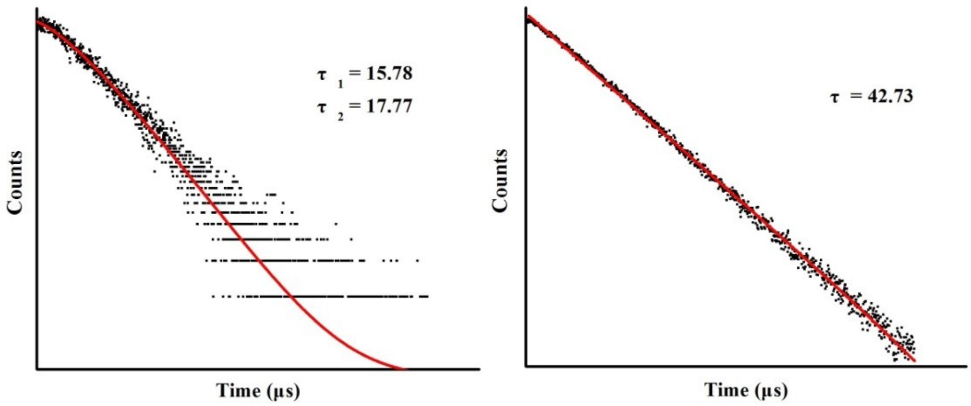



**Fig.S4** The excitation spectra of complexes **1**, **2** and **4** in the solid state.




(a) (b)

**Fig.S5** (a) Luminescence decay profile for complex **1** in the solid state; (b) Luminescence decay profile for doped complex $\mathbf{Sm_{0.4}Gd_{0.6}DBM}$ in the solid state.

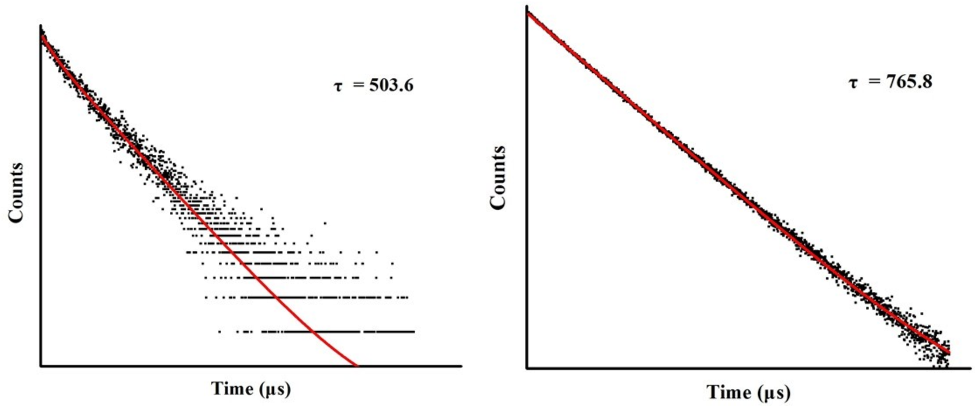
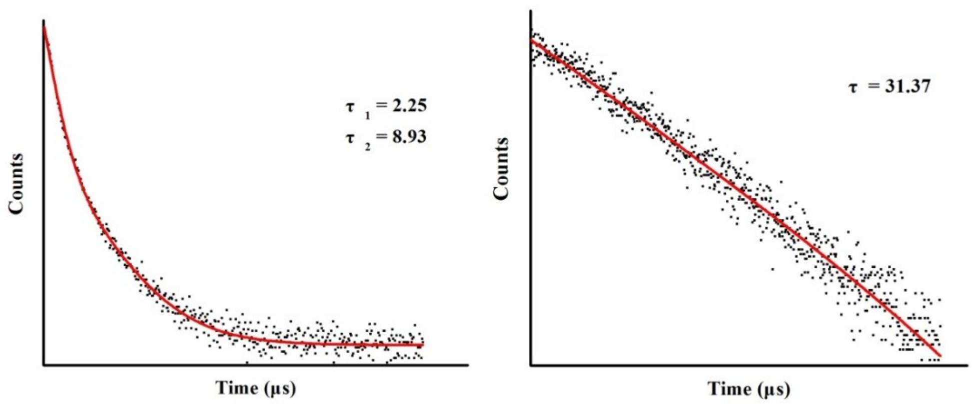



**Fig.S6** (a) Luminescence decay profile for complex **2** in the solid state; (b) Luminescence decay profile for doped complex $\mathbf{Eu_{0.22}Gd_{0.78}DBM}$ in the solid state.




(a) (b)

**Fig.S7** (a) Luminescence decay profile for complex **4** in the solid state; (b) Luminescence decay profile for doped complex $\mathbf{Yb_{0.1}Gd_{0.9}DBM}$ in the solid state.

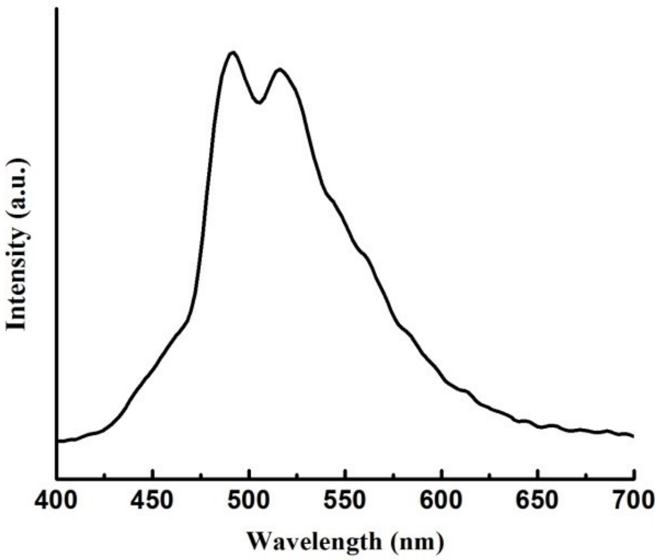



**Fig.S8** Phosphorescence spectrum of $Gd_2L_2(DBM)_4(OAc)_2$ (**3**) at 77K.

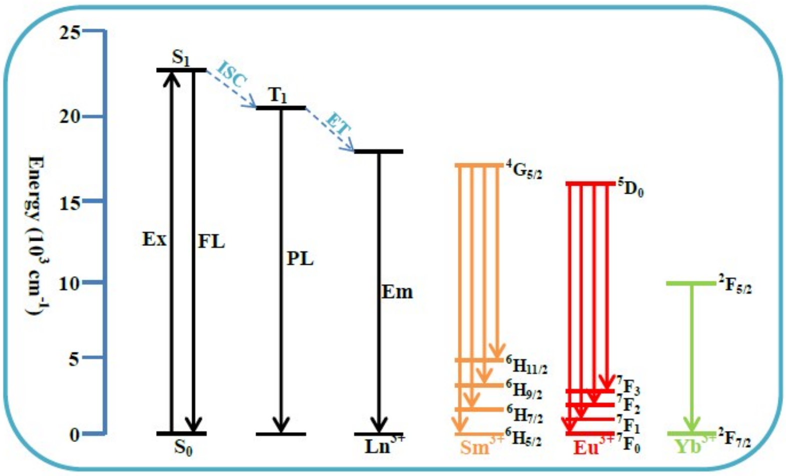



**Fig.S9** Schematic energy level diagram and energy transfer processes.$S_1$: first excited singlet state and $T_1$: first excited triplet state.

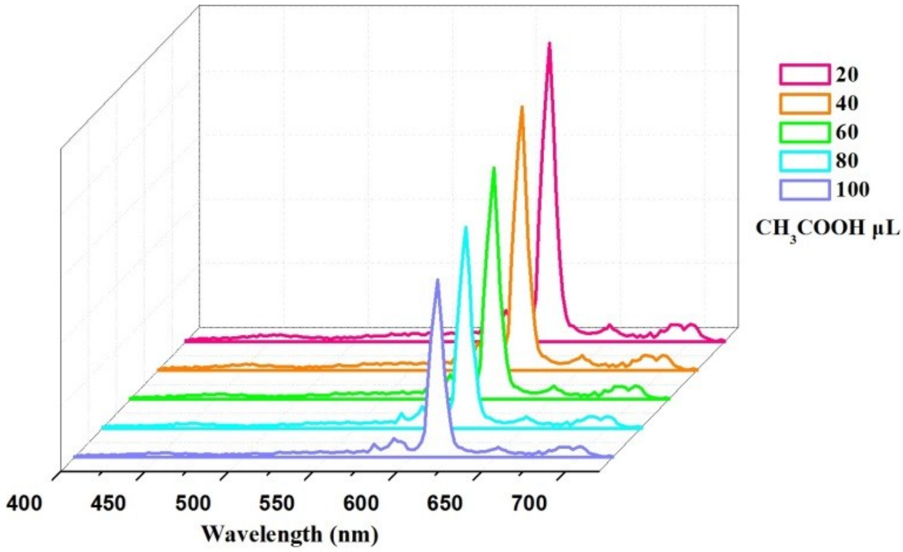



**Fig.S10** Emission spectra of doped complex **$Eu_{0.4}Gd_{0.6}DBM$** upon incremental addition of acetic acid.

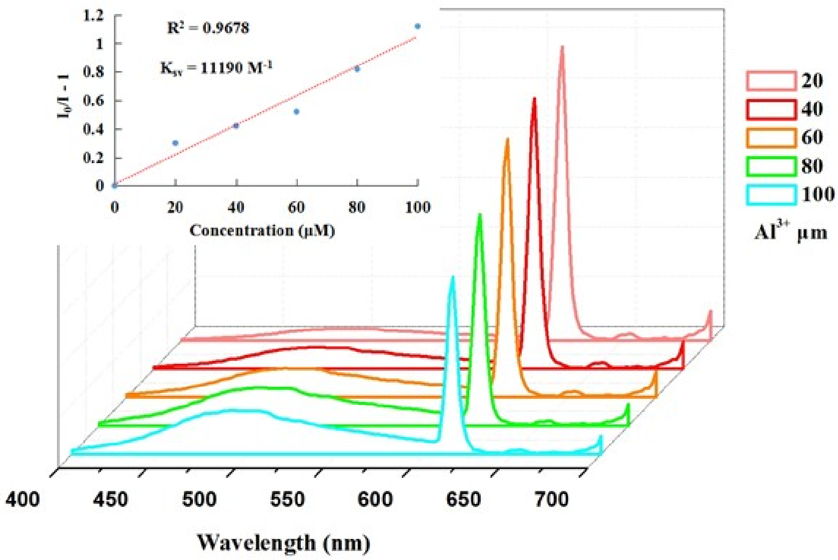



**Fig.S11** Emission spectra of doped complex **$Eu_{0.4}Gd_{0.6}DBM$** with increasing concentration of $Al^{3+}$.

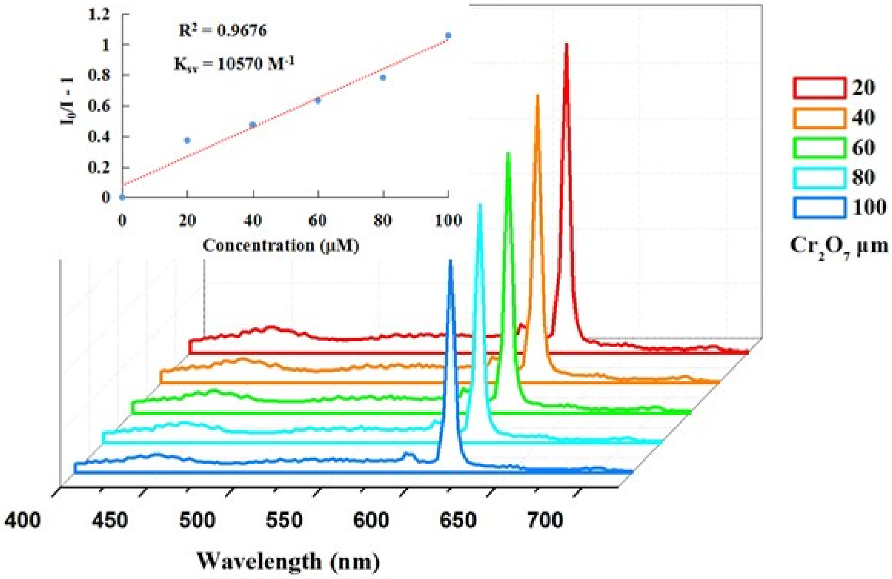
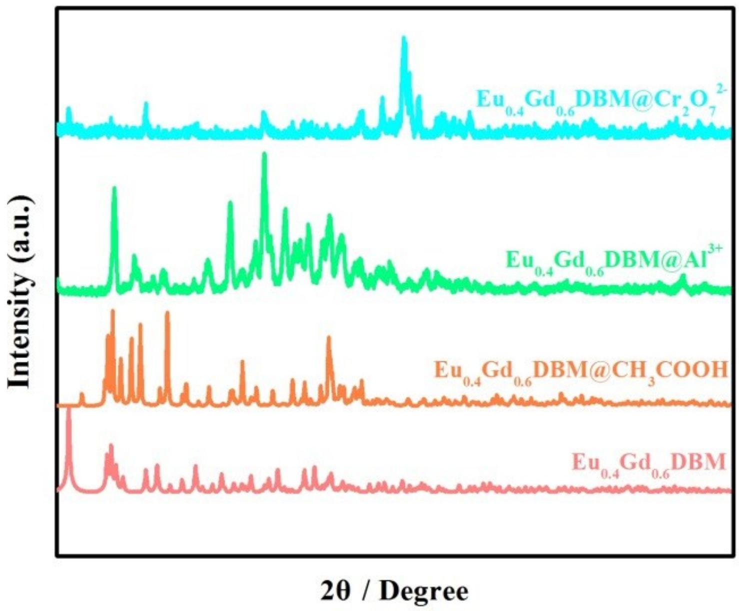
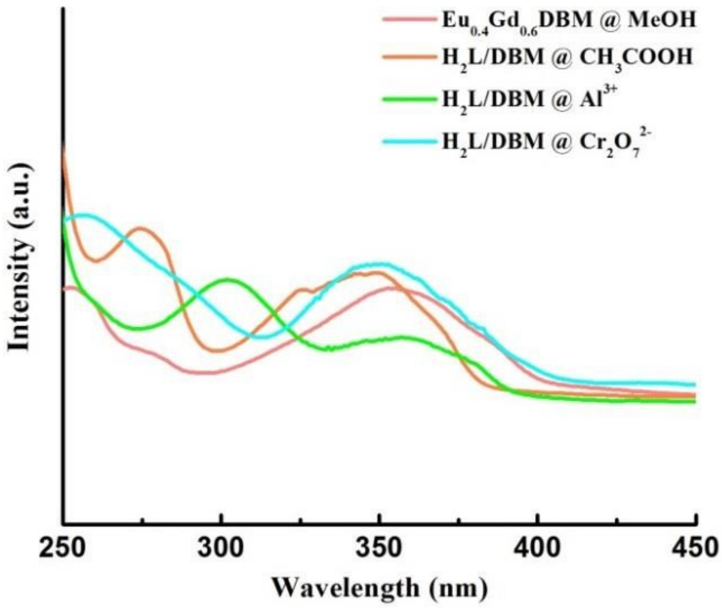



**Fig.S12** Emission spectra of complex **$Eu_{0.4}Gd_{0.6}$DBM** with increasing concentration of $Cr_2O_7^{2-}$.




(a)




(b)

**Fig.S13** (a) PXRD patterns for $\mathbf{Eu_{0.4}Gd_{0.6}DBM}$@$CH_3COOH$, $Al^{3+}$ and $Cr_2O_7^{2-}$; (b) UV-vis absorption spectra of $\mathbf{Eu_{0.4}Gd_{0.6}DBM}$@MeOH, $H_2L$@$CH_3COOH$, $Al^{3+}$ and $Cr_2O_7^{2-}$.

**Table S1** Elemental analysis of lanthanide ions by ICP for doped complexes $\mathbf{Ln_xGd_{1-x}DBM}$

| Complex | $Eu_{0.22}Gd_{0.78}DBM$ | | $Sm_{0.4}Gd_{0.6}DBM$ | | $Yb_{0.1}Gd_{0.9}DBM$ | |
|---|---|---|---|---|---|---|
| | Sm | Gd | Eu | Gd | Yb | Gd |
| Wt % (Found) | 40.0 | 60.0 | 22.0 | 78.0 | 10.0 | 90.0 |
| Mol% | 40.3 | 59.7 | 21.2 | 78.8 | 9.1 | 90.9 |

**Table S2** $(Ln_xGd_{1-x})_2L_2(DBM)_4(OAc)_2$ – luminescence intensity ratio, lifetime and quantum yield of $Ln^{3+}$ ions in corresponding doped materials.

| $Ln^{3+}$ | $Sm^{3+}$(**1**) | $Eu^{3+}$(**2**) | $Yb^{3+}$(**4**) |
|---|---|---|---|
| $I/I_0$ | 1.44 | 1.60 | 2.35 |
| $\tau_0$ (μs) | 15.78 / 17.77 | 503.60 | 2.25 / 8.93 |
| $\tau$ (μs) | 42.73 | 765.8 | 31.37 |
| $\varphi_0$ (%) | 1.5 | 62.7 | — |
| $\varphi$ (%) | 4.2 | 73.5 | — |

$I_0$, $\tau_0$, $\varphi_0$: $Ln_2L_2(DBM)_4(OAc)_2$**;** I, τ, φ: doped materials – $Eu_{0.4}Gd_{0.6}$DBM, $Sm_{0.4}Gd_{0.6}$DBM and $Yb_{0.1}Gd_{0.9}$DBM.

**Table S3** The triplet energy levels of $H_2L$/DBM and the energy gaps $\Delta E(T_1–Ln^{3+})$

| | $T_1$ | $Eu^{3+}$ | $Sm^{3+}$ | $Yb^{3+}$ |
|---|---|---|---|---|
| Energy level ($cm^{-1}$) | 20366 | 17500 | 17924 | 10000 |
| $\Delta E(T_1 – Ln^{3+})$ | — | 2866 | 2442 | 10366 |

**Table S4** Elemental analysis of lanthanide ions by ICP for doped materials in target cations

| Complex | $Eu_{0.4}Gd_{0.6}DBM@Al^{3+}$ | |
|---|---|---|
| | Al | Eu/Gd |
| Mol% | 48.3 | 51.7 |