Improved luminescence properties by self-assembly of lanthanide compounds with 1-D chain structure for sensing of CH_3COOH and toxic HS^- anions

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Synthesis of complexes 1, 3, 4 and doped compounds

$[Sm_2L(TTA)_4(OAc)_2]_n$ (1). Yield: 0.169g (45.7%). Elemental analysis (%) calcd for $C_{28}H_{22}F_6GdNO_7S_2$ (812.95): C, 41.33; H, 2.71; N, 1.72. found: C, 41.30； H, 2.70; N, 1.73; IR (KBr, cm^{-1}): 3058 (w), 2946 (s), 2733 (w), 2690(w), 1692 (vs), 1684 (vs), 1532 (s), 1431 (vs), 1302 (s), 1245 (vs), 1156 (m), 1104 (m), 961 (vs), 884 (w), 722 (m), 643 (w), 589 (m). UV−vis [MeOH, λ]: 211, 254, 348 nm.

$[Gd_2L(TTA)_4(OAc)_2]_n$ (3). Yield: 0.176g (47.2%). Elemental analysis (%) calcd for $C_{28}H_{22}F_6GdNO_7S_2$ (819.84): C, 40.98; H, 2.68; N, 1.71. found: C, 41.00； H, 2.67; N, 1.70; IR (KBr, cm^{-1}): 3062 (w), 2945 (s), 2734 (w), 2688(w), 1689 (vs), 1684 (vs), 1534 (s), 1429 (vs), 1299 (s), 1240 (vs), 1154 (m), 1103 (m), 962 (vs), 885 (w), 721 (m), 642 (w), 590 (m). UV−vis [MeOH, λ]: 211, 254, 348 nm.

$[Yb_2L(TTA)_4(OAc)_2]_n$ (4). Yield: 0.181g (48.2%). Elemental analysis (%) calcd for $C_{28}H_{22}F_6GdNO_7S_2$ (835.63): C, 40.21; H, 2.63; N, 1.68. found: C, 41.19； H, 2.63; N, 1.67; IR (KBr, cm^{-1}): 3058 (w), 2941 (s), 2728 (w), 2692(w), 1687 (vs), 1681 (vs), 1538 (s), 1432 (vs), 1296 (s), 1242 (vs), 1151 (m), 1101 (m), 963 (vs), 882 (w), 720 (m), 644 (w), 590 (m). UV−vis [MeOH, λ]: 211, 254, 348 nm.

$[(Sm_xGd_{1-x})_2L(TTA)_4(OAc)_2]_n$ IR (KBr, cm^{-1}): 3060 (w), 2950 (s), 2740 (w), 2691(w), 1692 (vs), 1681 (vs), 1533 (s), 1435 (vs), 1301 (s), 1242 (vs), 1153 (m), 1098 (m), 962 (vs), 880 (w), 719 (m), 645 (w), 583 (m). UV−vis [MeOH, λ]: 211, 254, 348 nm.

$[(Eu_xGd_{1-x})_2L(TTA)_4(OAc)_2]_n$ IR (KBr, cm^{-1}): 3055 (w), 2945 (s), 2736 (w), 2688(w), 1693 (vs), 1684 (vs), 1536 (s), 1430 (vs), 1303 (s), 1245 (vs), 1156 (m), 1105 (m), 963 (vs), 881 (w), 720 (m), 644 (w), 585 (m). UV−vis [MeOH, λ]: 211, 254, 348 nm.

$[(Yb_xGd_{1-x})_2L(TTA)_4(OAc)_2]_n$ IR (KBr, cm^{-1}): 3057 (w), 2946 (s), 2733 (w), 2687(w), 1691 (vs), 1682 (vs), 1538 (s), 1431 (vs), 1297 (s), 1246 (vs), 1154 (m), 1104 (m), 961(vs), 882 (w), 722 (m), 641 (w), 582 (m). UV−vis [MeOH, λ]: 211, 254, 348 nm.

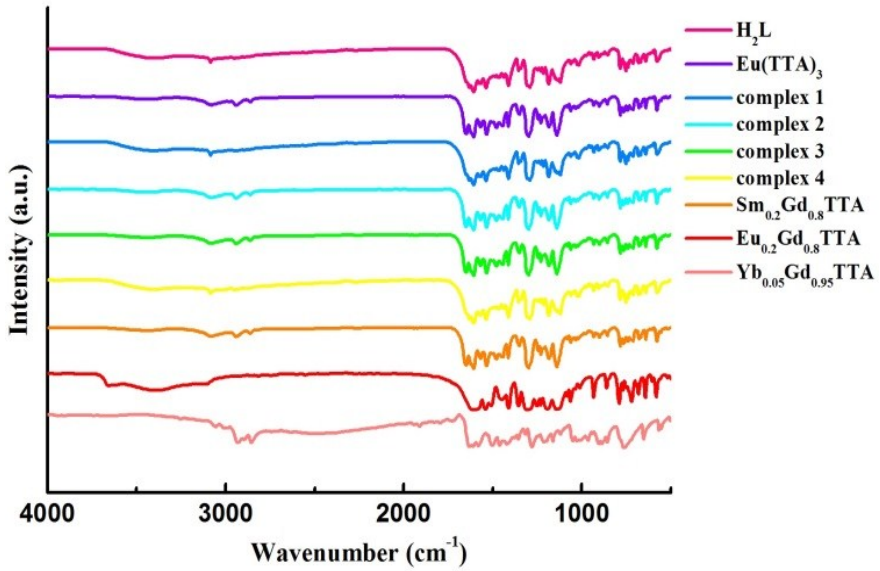


Fig.S1 IR spectra of H_2L, $Eu(TTA)_3$, complexes **1-4** and $Ln_xGd_{1-x}TTA$.

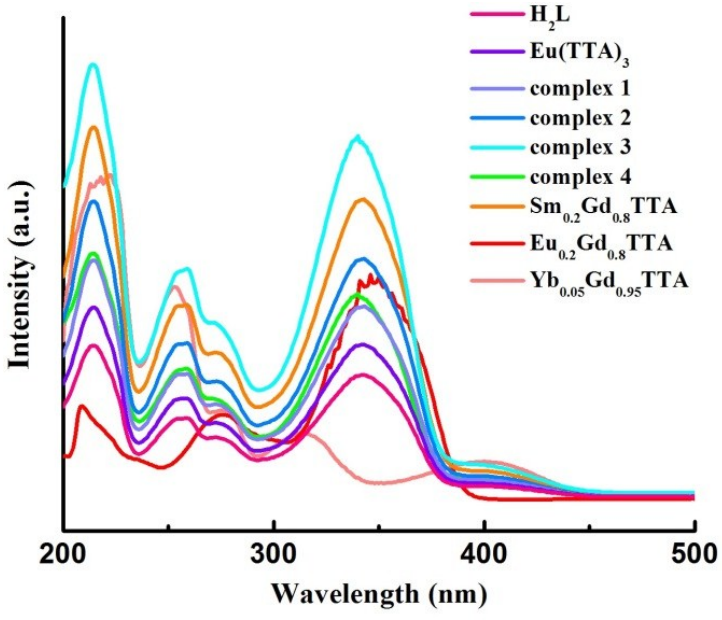


Fig.S2 UV-vis absorption spectra of H_2L, $Eu(TTA)_3$, complexes **1-4** and $Ln_xGd_{1-x}TTA$.

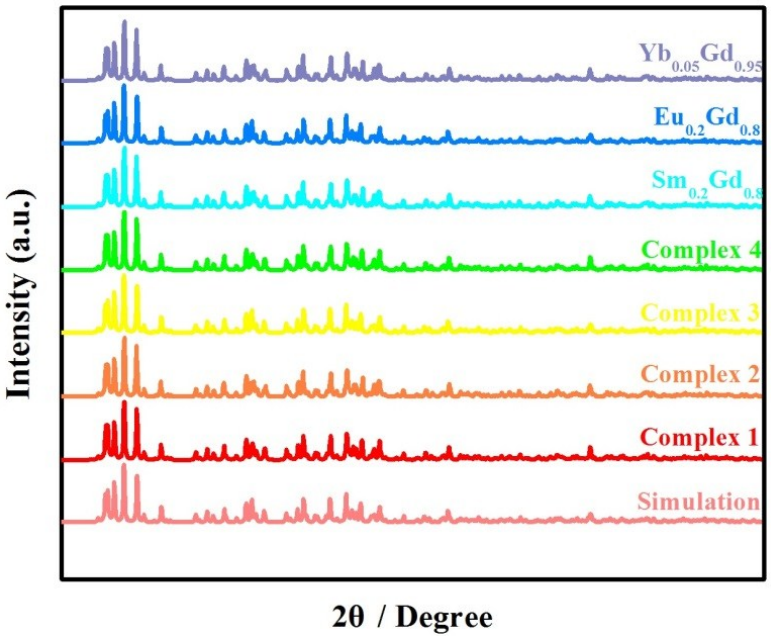


Fig.S3 PXRD patterns for simulation, complexes **1**-**4** and $Ln_xGd_{1-x}TTA$.

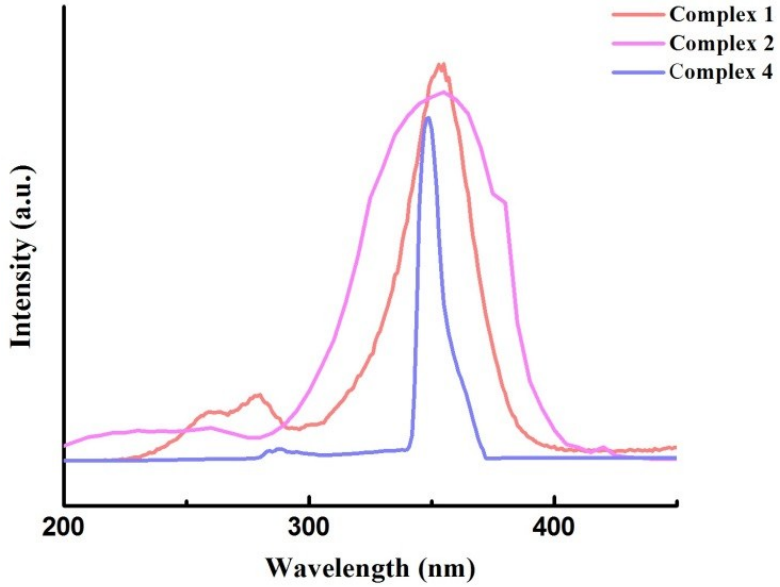
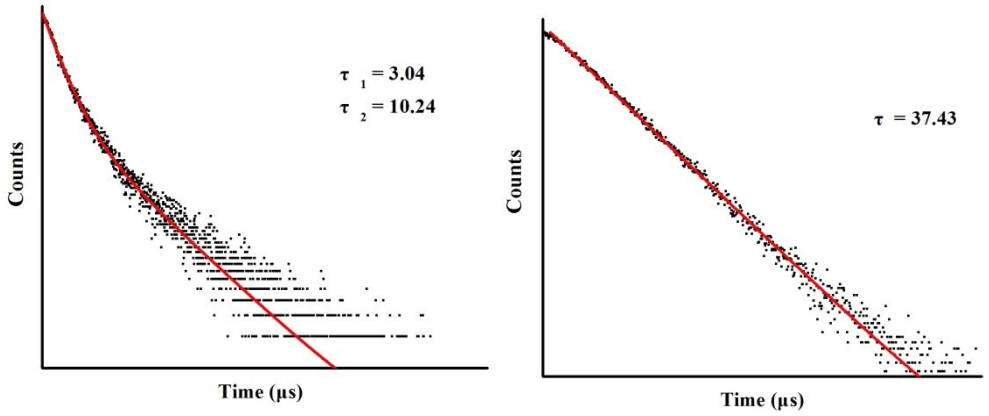
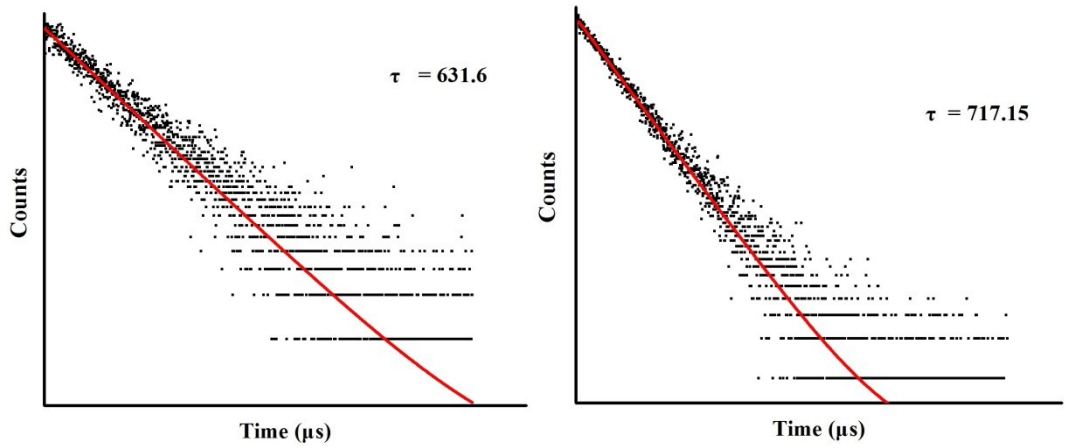


Fig.S4 The excitation spectra of complexes **1**, **2** and **4** in the solid state.



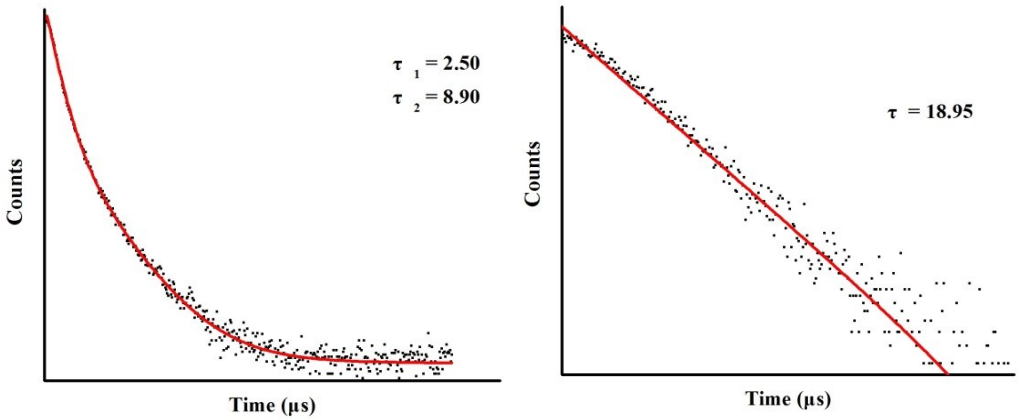
(a) (b)

Fig.S5 (a) Luminescence decay profile for complex **1** in the solid state; (b) Luminescence decay profile for doped complex $\mathbf{Sm_{0.2}Gd_{0.8}TTA}$ in the solid state.



(a) (b)

Fig.S6 (a) Luminescence decay profile for complex **2** in the solid state; (b) Luminescence decay profile for doped complex $\mathbf{Eu_{0.2}Gd_{0.8}TTA}$ 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 **$Yb_{0.05}Gd_{0.95}TTA$** in the solid state.

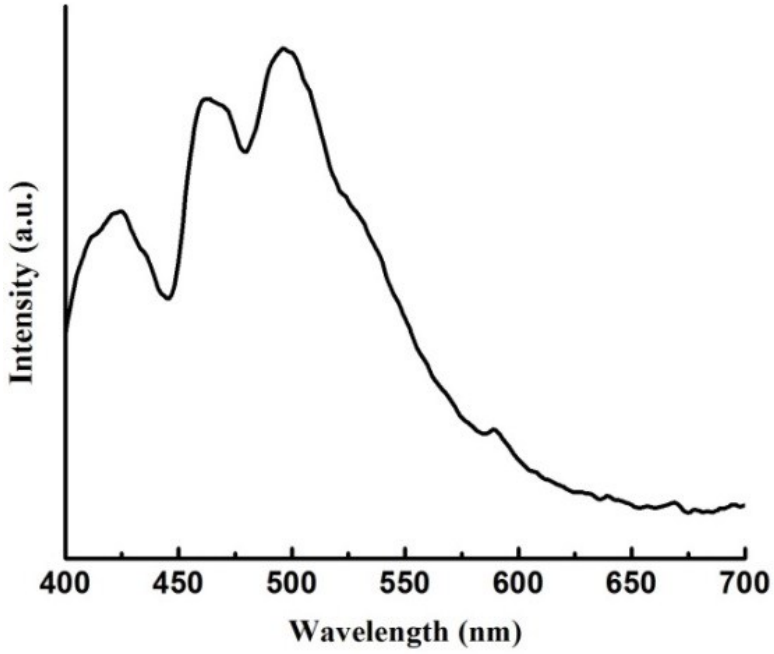
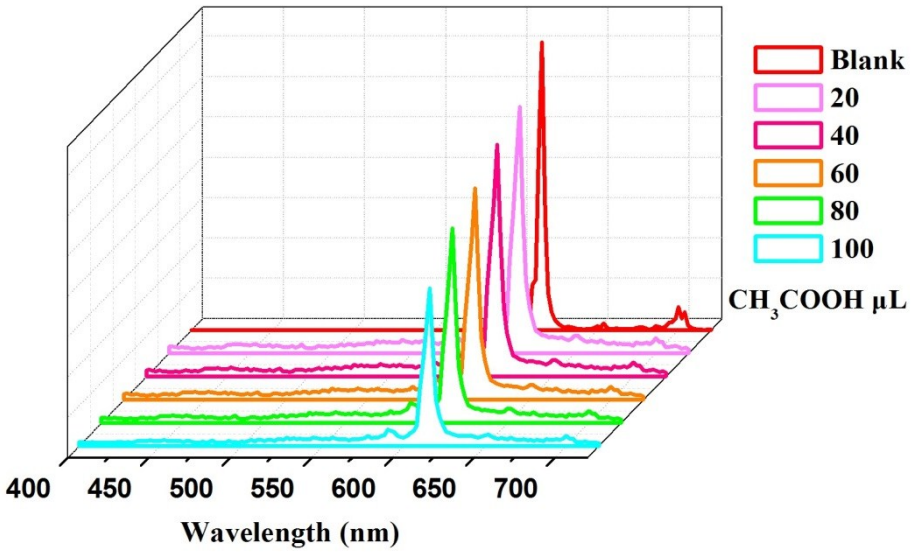
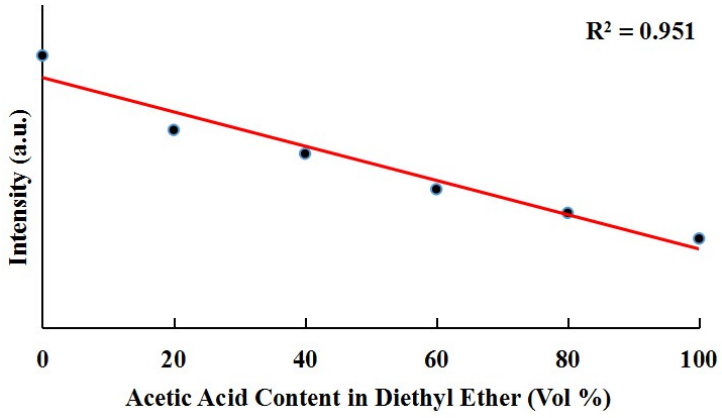


Fig.S8 Phosphorescence spectrum of $Gd_2L(TTA)_4(OAc)_2$ (**3**) at 77K.

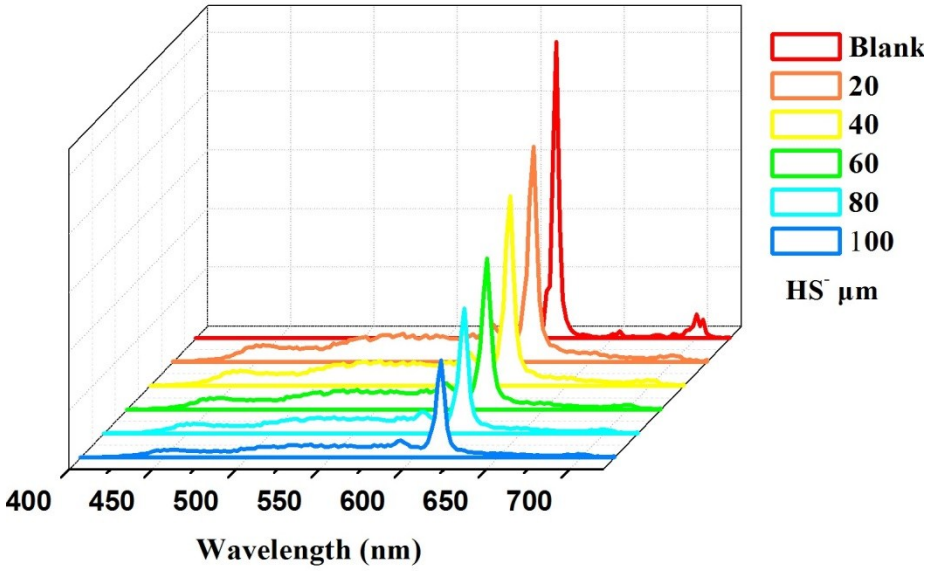


(a)

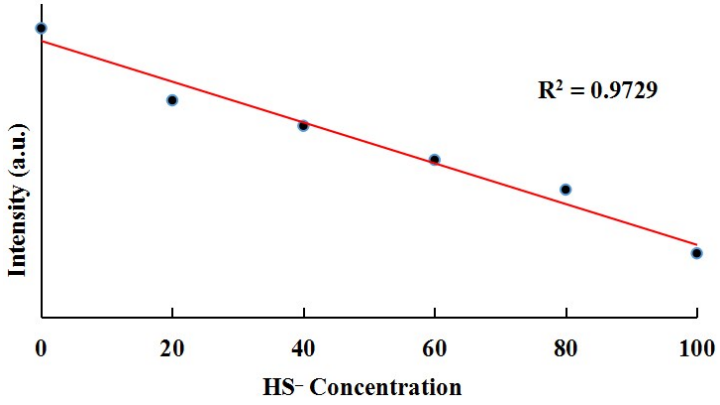


(b)

Fig.S9 (a) Emission spectra of doped complex **$Eu_{0.2}Gd_{0.8}TTA$** upon incremental addition of acetic acid; (b) The calibration curve with the addition of acetic acid.

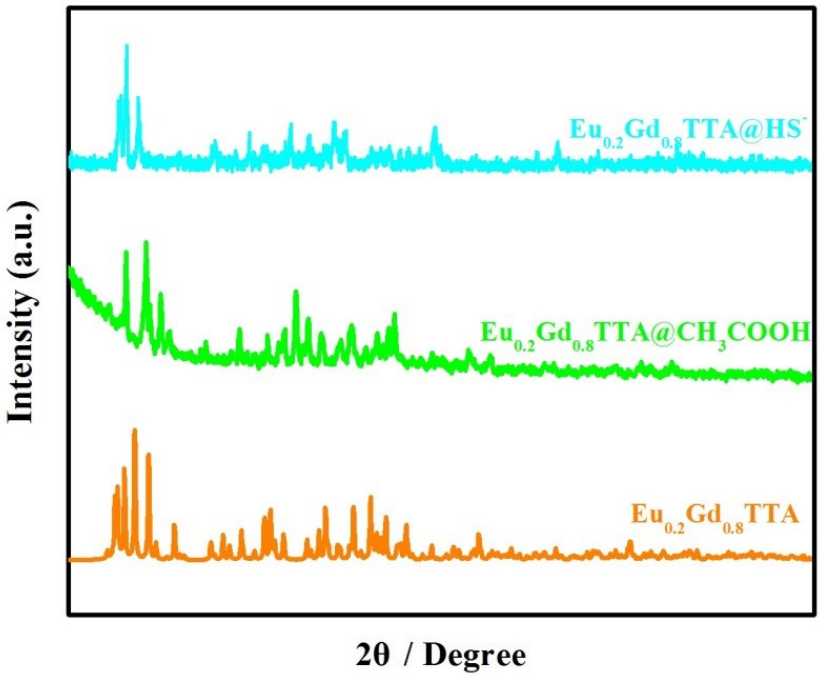


(a)

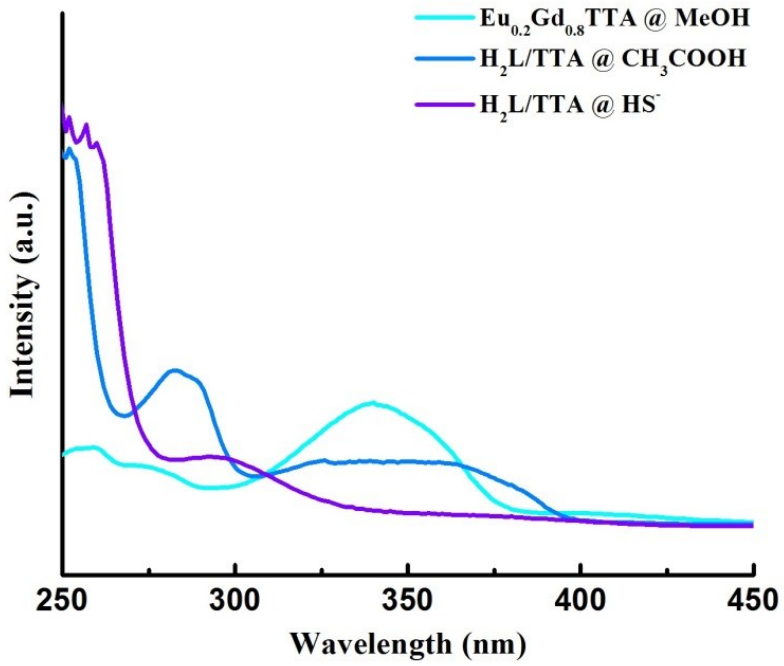


(b)

Fig.S10 (a) Emission spectra of complex **$Eu_{0.2}Gd_{0.8}TTA$** with increasing concentration of HS^-; (b) The calibration curve with increasing concentration of HS^- .



(a)



(b)

Fig.S11 (a) PXRD patterns for **$Eu_{0.2}Gd_{0.8}$TTA**@CH_3COOH and HS^-; (b) UV-vis absorption spectra of **$Eu_{0.2}Gd_{0.8}$TTA**@MeOH, H_2L/DBM@CH_3COOH and HS^-.

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

Complex	$Eu_{0.2}Gd_{0.8}TTA$		$Sm_{0.2}Gd_{0.8}TTA$		$Yb_{0.05}Gd_{0.95}TTA$	
	Sm	Gd	Eu	Gd	Yb	Gd
Wt % (Found)	20.0	80.0	20.0	80.0	5.0	95.0
Mol%	19.2	80.8	18.9	81.1	4.4	95.6

Table S2 $\mathbf{[(Ln_xGd_{1-x})_2L(TTA)_4(OAc)_2]_n}$ – 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	3.68	3.43	3.8
τ_0 (μs)	3.04 / 10.24	631.60	2.50 / 8.90
τ (μs)	37.43	717.15	18.95
φ_0 (%)	1.1	53.9	—
φ (%)	6.8	76.2	—

I_0, τ_0, φ_0: $Ln_2L_2(DBM)_4(OAc)_2$**;** I, τ, φ: doped materials –$Eu_{0.2}Gd_{0.8}TTA$, $Sm_{0.2}Gd_{0.8}TTA$ and $Yb_{0.05}Gd_{0.95}TTA$

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

	T_1	Eu^{3+}	Sm^{3+}	Yb^{3+}
Energy level (cm^{-1})	20161	17500	17924	10000
$\Delta E(T_1 – Ln^{3+})$	—	2661	2237	10161