New Journal of Chemistry

Supporting information

Synthesis and luminescence studies of lanthanide complexes (Gd, Dy, Tb) with phenyl- and 2-pirydylthiolates supported by bulky β-diketiminate ligand. Impact of ligand environment on terbium(III) emission

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1. X-ray structural determination

Table S1. Crystallographic data for the compounds.

Compound	$\mathbf{1}^{Gd}\cdot$thf	$\mathbf{1}^{Tb}$	$\mathbf{1}^{Tb}$**(super)**	$\mathbf{1}^{Dy}\cdot$0.5thf	$\mathbf{2}^{Tb}$	$\mathbf{2}^{Dy}$	$\mathbf{4}^{Tb}\cdot 2C_7H_8$	$\mathbf{3}^{Dy}\cdot$0.34thf
Empirical formula	$C_{41}H_{65}GdI_2N_2O_3$	$C_{37}H_{57}I_2N_2O_2Tb$	$C_{37}H_{57}I_2N_2O_2Tb$	$C_{35}H_{53}DyI_2N_2O_{1.5}$	$C_{45}H_{59}N_2OS_2Tb$	$C_{44.84}H_{58.87}DyI_{0.03}N_2OS_{1.98}$	$C_{96}H_{118}N_4S_4Tb_2$	$C_{40.38}H_{51.76}DyN_4O_{0.34}S_2$
Formula weight	1045.00	974.56	974.56	942.09	866.98	870.94	1774.02	825.28
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	$P2_1/m$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	10.2426(4)	12.7128(5)	19.1978(6)	31.9845(6)	11.1634(4)	11.1737(3)	11.4580(6)	12.8956(5)
b/Å	20.0490(9)	19.5799(6)	19.5799(6)	12.1125(3)	11.3600(5)	11.3349(4)	14.6416(7)	19.6998(7)
c/Å	10.6372(7)	16.8372(5)	22.8398(8)	21.4148(5)	18.3231(9)	18.2940(5)	15.2678(6)	15.2240(7)
α/°	90	94.1500(10)	102.7210(10)	90	88.633(2)	88.5000(10)	92.345(2)	90
β/°	92.955(2)	79.6990(10)	106.1380(10)	116.2470(10)	81.303(2)	81.1760(10)	111.744(2)	93.257(2)
γ/°	90	107.4440(10)	97.7610(10)	90	65.0100(10)	65.0310(10)	111.629(2)	90
Volume/Å^3	2181.49(19)	3933.1(2)	7866.1(4)	7441.0(3)	2079.83(16)	2073.65(11)	2164.40(18)	3861.3(3)
Z	2	4	8	8	2	2	1	4
ρ_{calc}g/cm^3	1.591	1.646	1.646	1.682	1.384	1.395	1.361	1.420
μ/mm^{-1}	2.971	3.399	3.399	3.697	1.836	1.955	1.764	2.077
F(000)	1038.0	1920.0	3840.0	3688.0	896.0	898.0	916.0	1691.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.982 to 49.228	3.254 to 52.896	1.928 to 52.9	3.894 to 52.954	4.076 to 52.962	4.072 to 55.888	4.004 to 55.83	3.384 to 51.456
Index ranges	$-10 \le h \le 12$, $-22 \le k \le 19$, $-11 \le l \le 5$	$-15 \le h \le 15$, $-22 \le k \le 24$, $-21 \le l \le 16$	$-24 \le h \le 24$, $-23 \le k \le 24$, $-28 \le l \le 27$	$-40 \le h \le 33$, $-15 \le k \le 11$, $-23 \le l \le 26$	$-12 \le h \le 13$, $-13 \le k \le 14$, $-22 \le l \le 22$	$-14 \le h \le 14$, $-14 \le k \le 14$, $-24 \le l \le 21$	$-15 \le h \le 15$, $-19 \le k \le 19$, $-20 \le l \le 13$	$-15 \le h \le 15$, $-22 \le k \le 24$, $-18 \le l \le 14$
Reflections collected	5152	35394	71164	24646	16619	17676	36467	29367
Independent reflections	2613 [R_{int} = 0.0195, R_{sigma} = 0.0293]	16094 [R_{int} = 0.0258, R_{sigma} = 0.0435]	32268 [R_{int} = 0.0329, R_{sigma} = 0.0607]	7616 [R_{int} = 0.0317, R_{sigma} = 0.0389]	8512 [R_{int} = 0.0237, R_{sigma} = 0.0412]	9547 [R_{int} = 0.0176, R_{sigma} = 0.0286]	10281 [R_{int} = 0.0315, R_{sigma} = 0.0306]	7362 [R_{int} = 0.0301, R_{sigma} = 0.0325]
Restraints/parameters	27/238	90/860	118/1663	21/385	7/479	7/484	384/675	6/446
Goodness-of-fit on F^2	1.035	1.021	1.015	1.032	1.047	1.045	1.046	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0249, wR_2 = 0.0560	R_1 = 0.0404, wR_2 = 0.0881	R_1 = 0.0459, wR_2 = 0.0993	R_1 = 0.0274, wR_2 = 0.0502	R_1 = 0.0252, wR_2 = 0.0521	R_1 = 0.0195, wR_2 = 0.0434	R_1 = 0.0193, wR_2 = 0.0449	R_1 = 0.0239, wR_2 = 0.0463
Final R indexes [all data]	R_1 = 0.0290, wR_2 = 0.0579	R_1 = 0.0564, wR_2 = 0.0959	R_1 = 0.0906, wR_2 = 0.1202	R_1 = 0.0367, wR_2 = 0.0530	R_1 = 0.0297, wR_2 = 0.0539	R_1 = 0.0217, wR_2 = 0.0441	R_1 = 0.0220, wR_2 = 0.0460	R_1 = 0.0330, wR_2 = 0.0492
Largest diff. peak/hole / e Å^{-3}	0.64/-0.66	2.02/-2.17	1.67/-1.12	0.87/-0.90	0.62/-0.42	0.42/-0.46	0.63/-0.36	0.42/-0.41

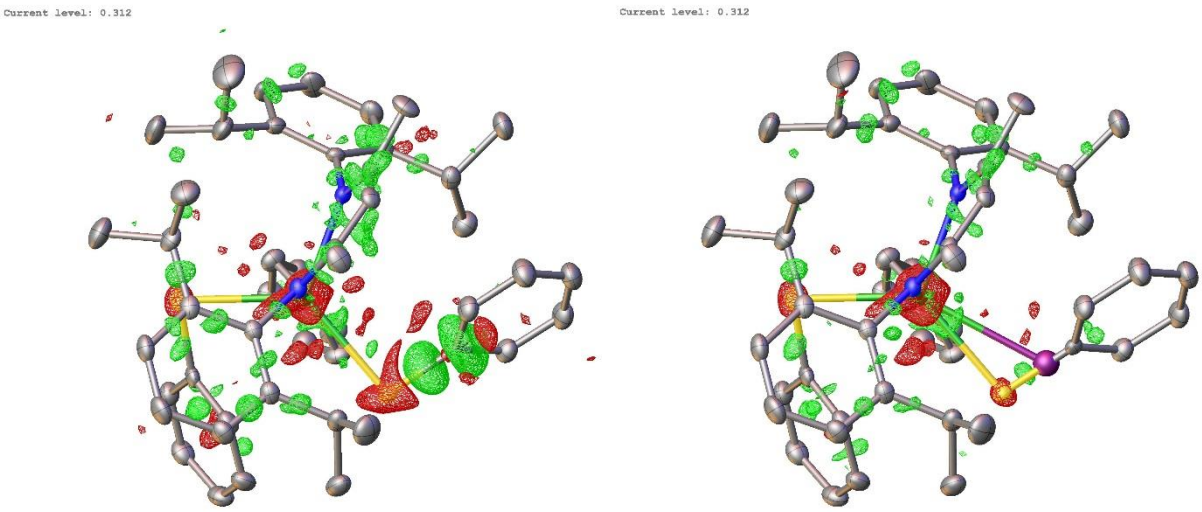

Fig. S1. Left – the residual electron density map (0.31 eÅ^{-3} level) for a model [Dy(^{dipp}nacnac^{Me})(SPh)$_2$(thf)] (**2^{Dy}**) with full occupancy in complex **2^{Dy}**. Right – the residual electron density map for a model with partially occupied I (2.6%) and one of SPh (97.4%). Green and red area show excess or lack of electron density, respectively. Hydrogen atoms are not shown.

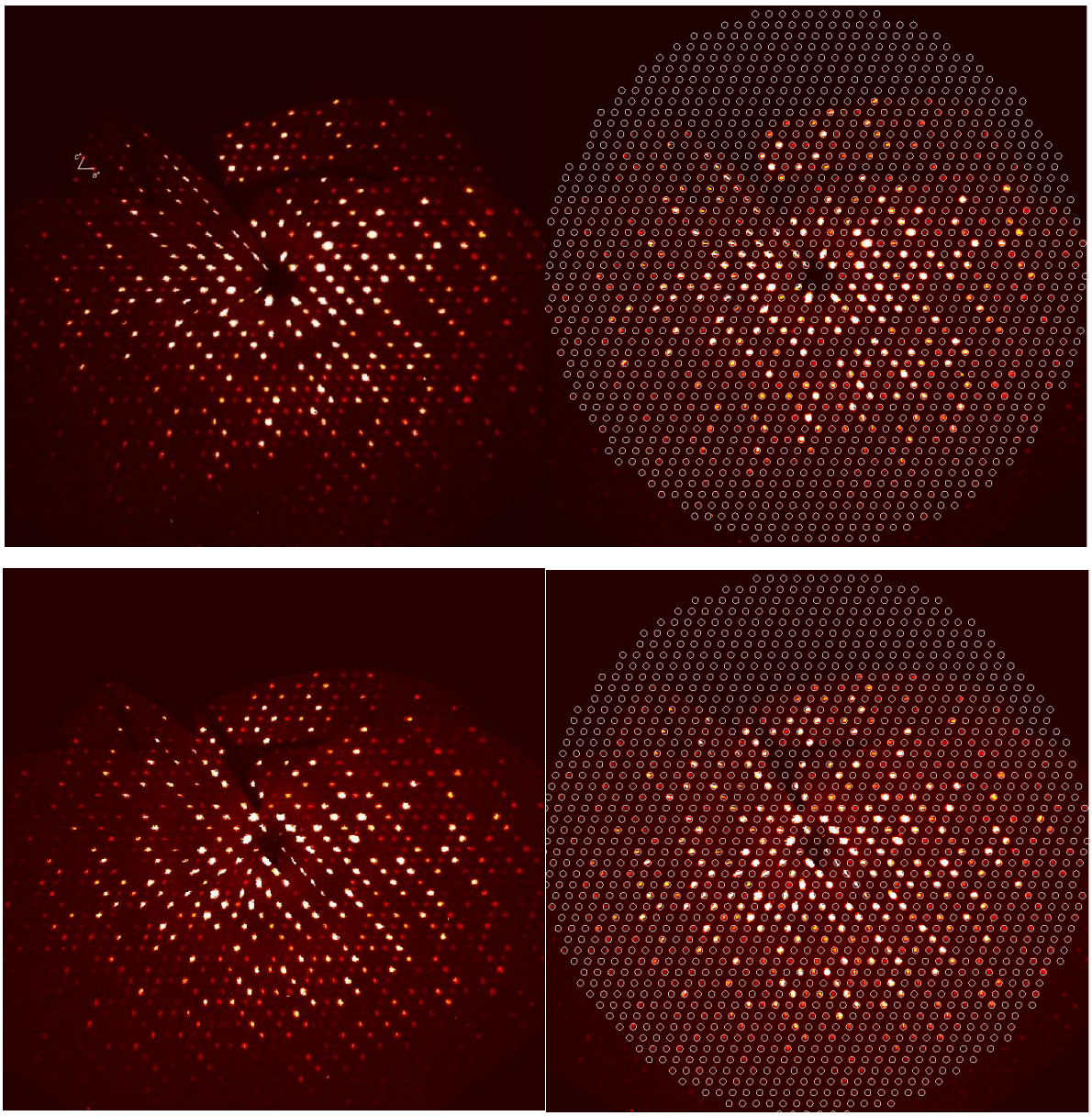

Fig. S2. Left – reciprocal space reconstructions for **1^{Tb}**, view of *h*0*l* (top) and *h*1*l* (bottom) layers (the thickness of the layers of 0.10 Å). Right – the corresponding reconstructions with calculated Bragg positions of reflections for the superstructure **1^{Tb}(super)** (the cell volume of 7866 Å^3).

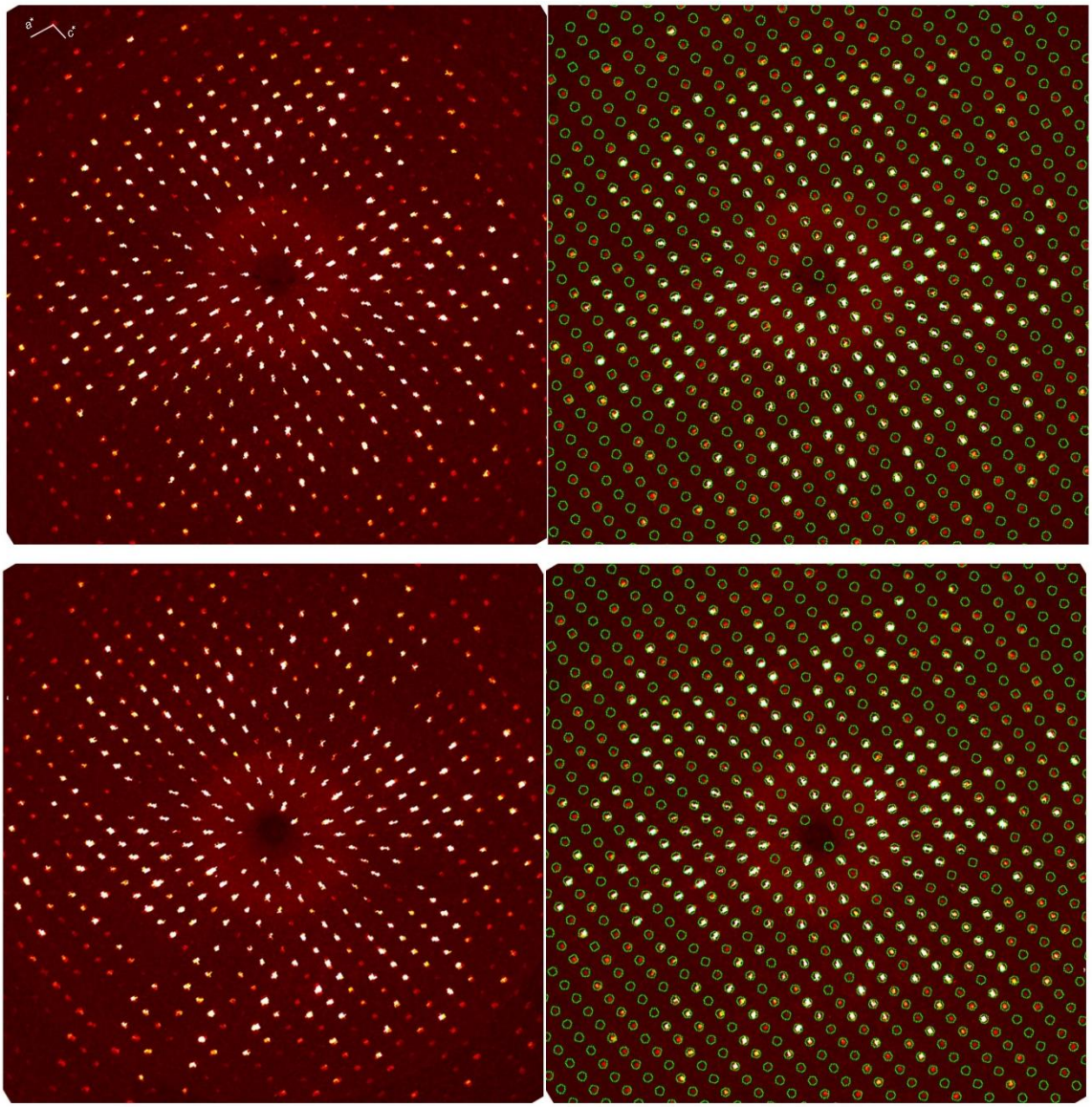

Fig. S3. Left – reciprocal space reconstructions for yet another single crystal of $\mathbf{1^{Tb}}$ that do not show superstructure reflections. View of *h*0*l* (top) and *h*1*l* (bottom) layers (the thickness of the layers of 0.10 Å). Right – the corresponding reconstructions with calculated Bragg positions of reflections for the substructure (the cell volume of 3910 $Å^3$).

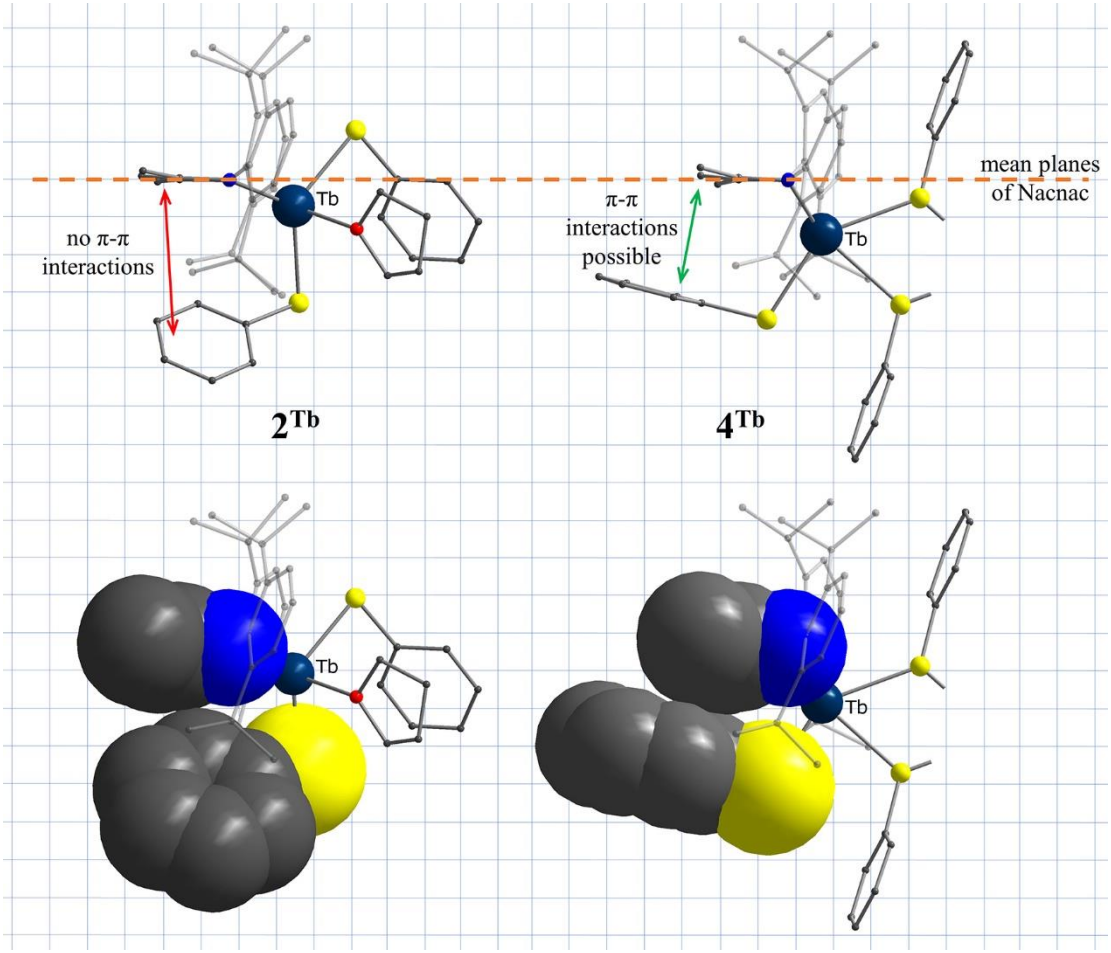

Fig. S4. Comparison of relative disposition of Nacnac⁻ and SPh⁻ ligands in the complexes $\mathbf{2^{Tb}}$ *(left)* and $\mathbf{4^{Tb}}$ *(right)* The complexes are arranged so that viewing direction goes through both N atoms of the Nacnac⁻ ligand and its mean plane (drawn through atoms N^1, N^2, C^1, C^3) is horisontal. Bottom row: the same disposition of the complexes with the closest Nacnac⁻ and SPh⁻ ligands shown in van der Waals spheres. Dipp moieties are simplified, the second half of the complex $\mathbf{4^{Tb}}$ is omitted. A grid with 1 Å spacing is shown in background.

2. Electronic absorption spectra

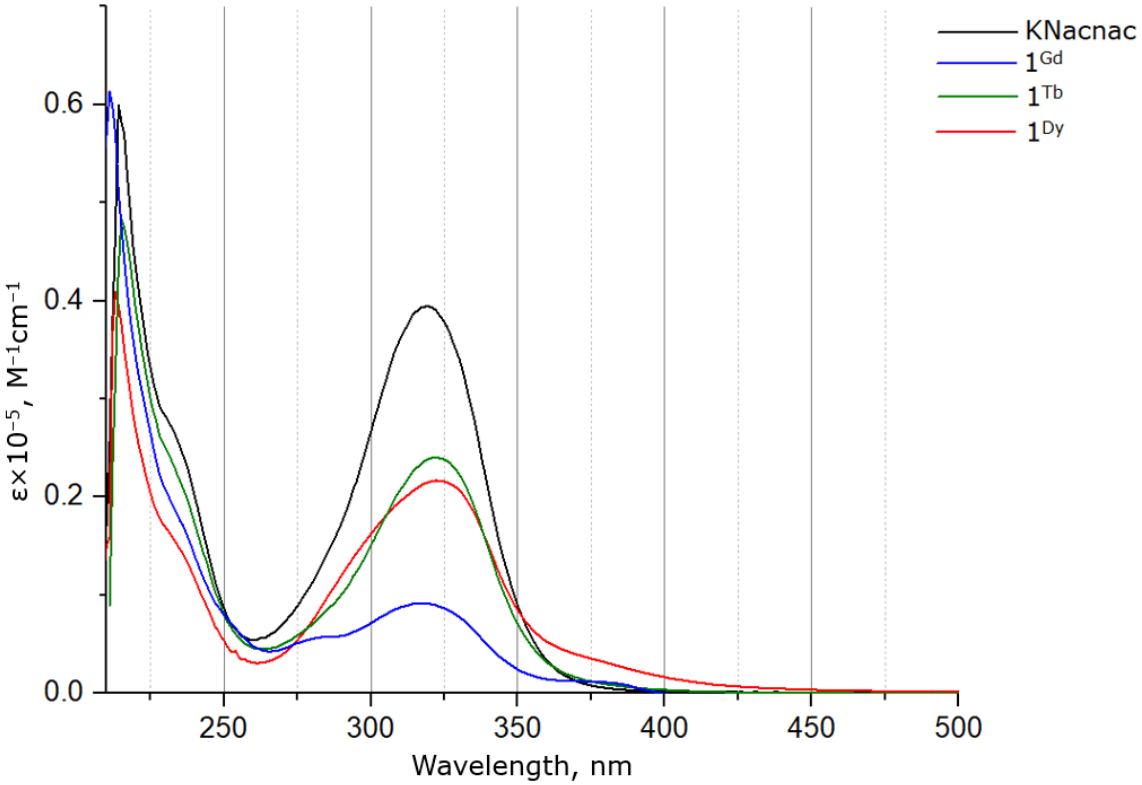

Fig. S5. Electronic absorption spectra of $\mathbf{1^{Ln}}$ and KNacnac in THF.

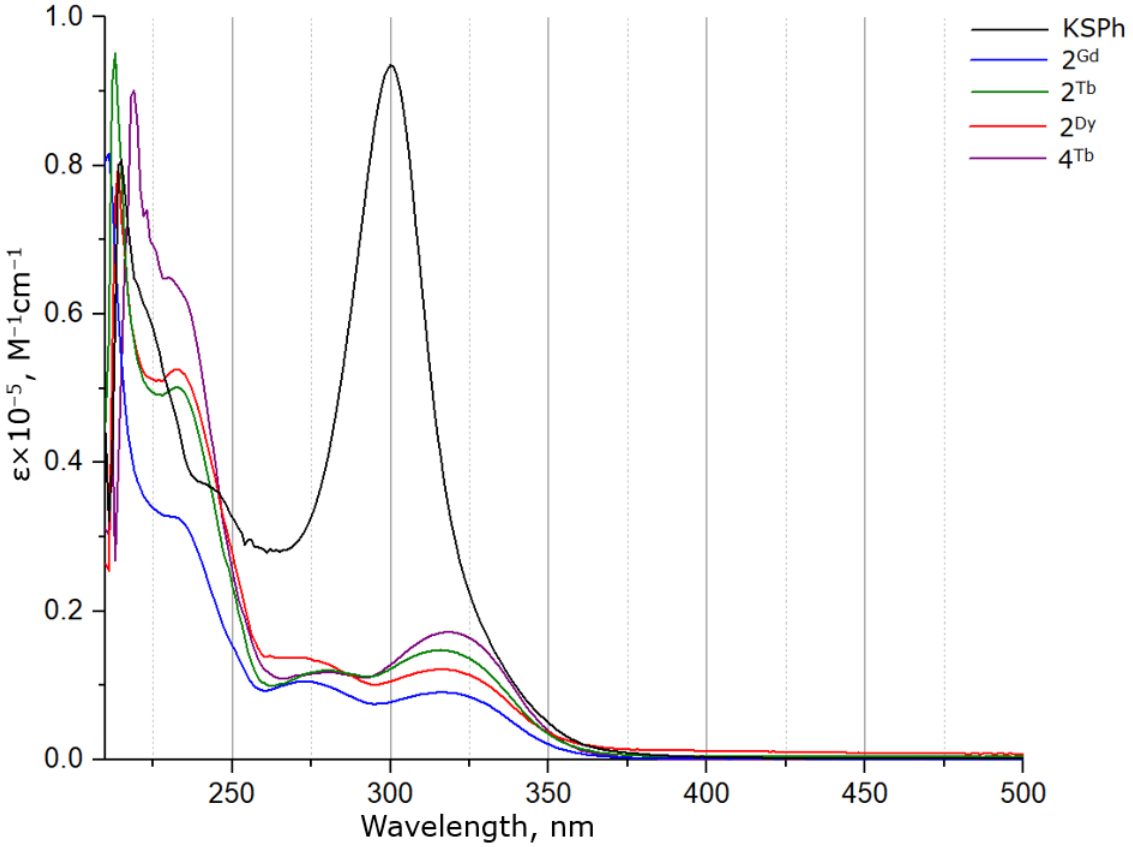

Fig. S6. Electronic absorption spectra of $\mathbf{2^{Ln}}$ and KSPh in THF, $\mathbf{4^{Tb}}$ in CH_2Cl_2. Molar extinction coefficient was not determined for KSPh due to its low solubility.

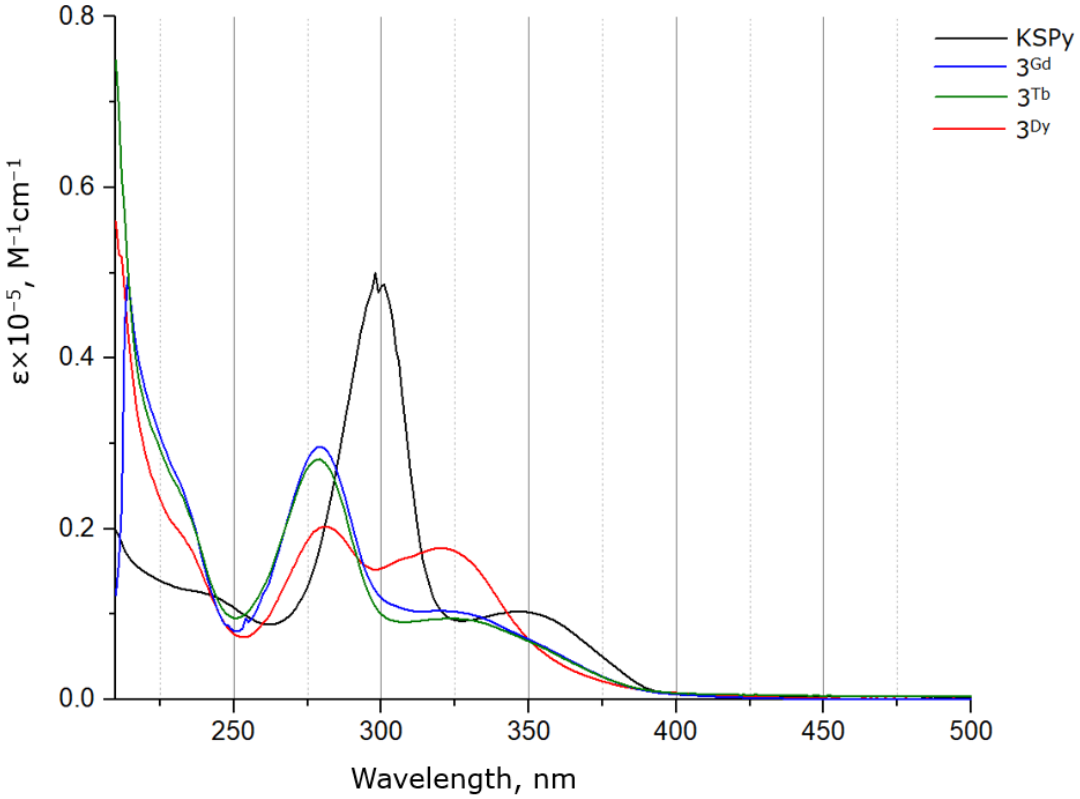

Fig. S7. Electronic absorption spectra of **3^{Ln}** and KSPy in THF. Molar extinction coefficient was not determined for KSPy due to its low solubility.

3. Luminescent study

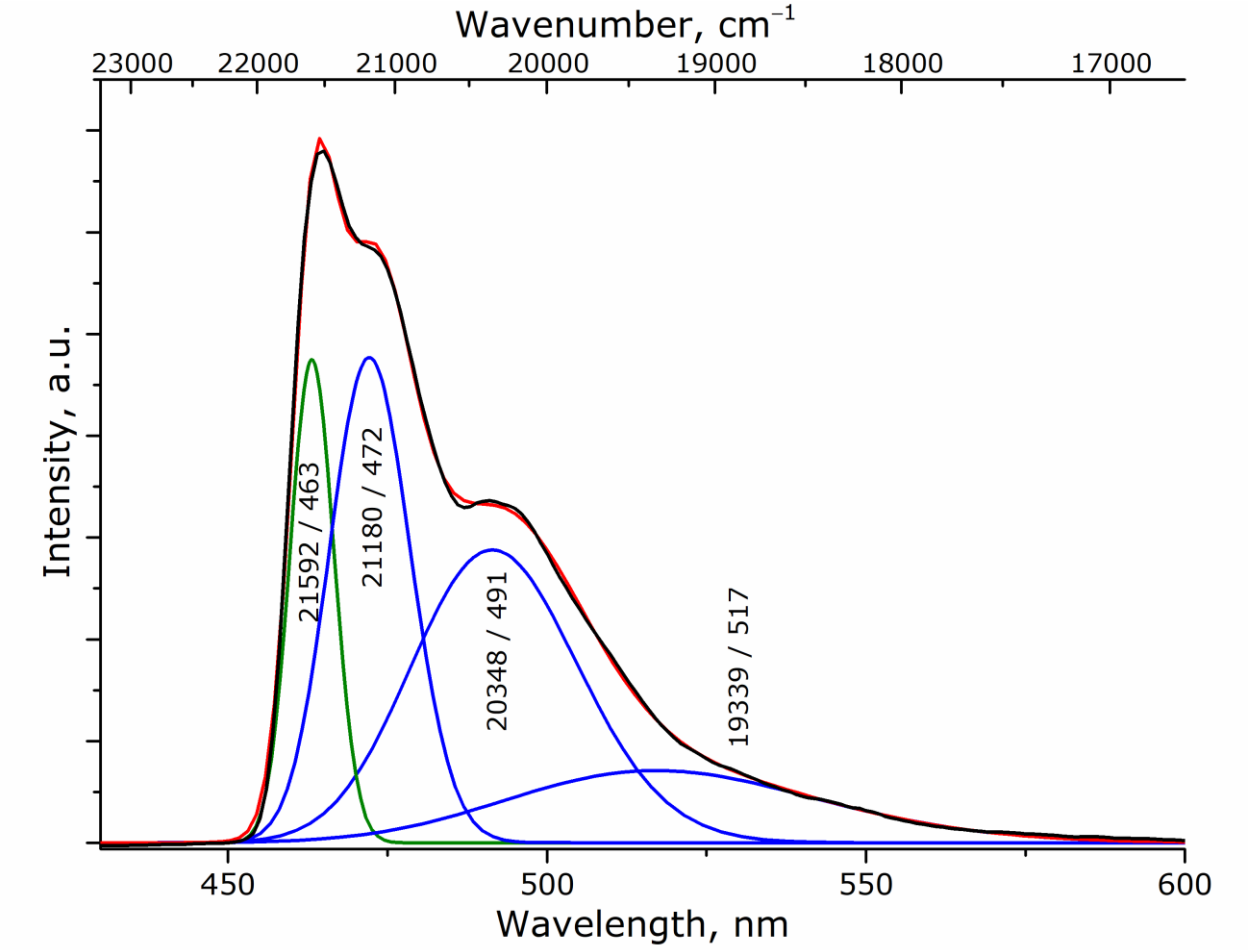

Fig. S8. Approximation of **3**^{Gd} PL spectrum obtained at 77 K by Gaussian curves (green and blue for separate peaks, red for the sum). The fitting is performed in the energy scale; fitted peak values are given as wavenumber, cm^{-1} / wavelength, nm

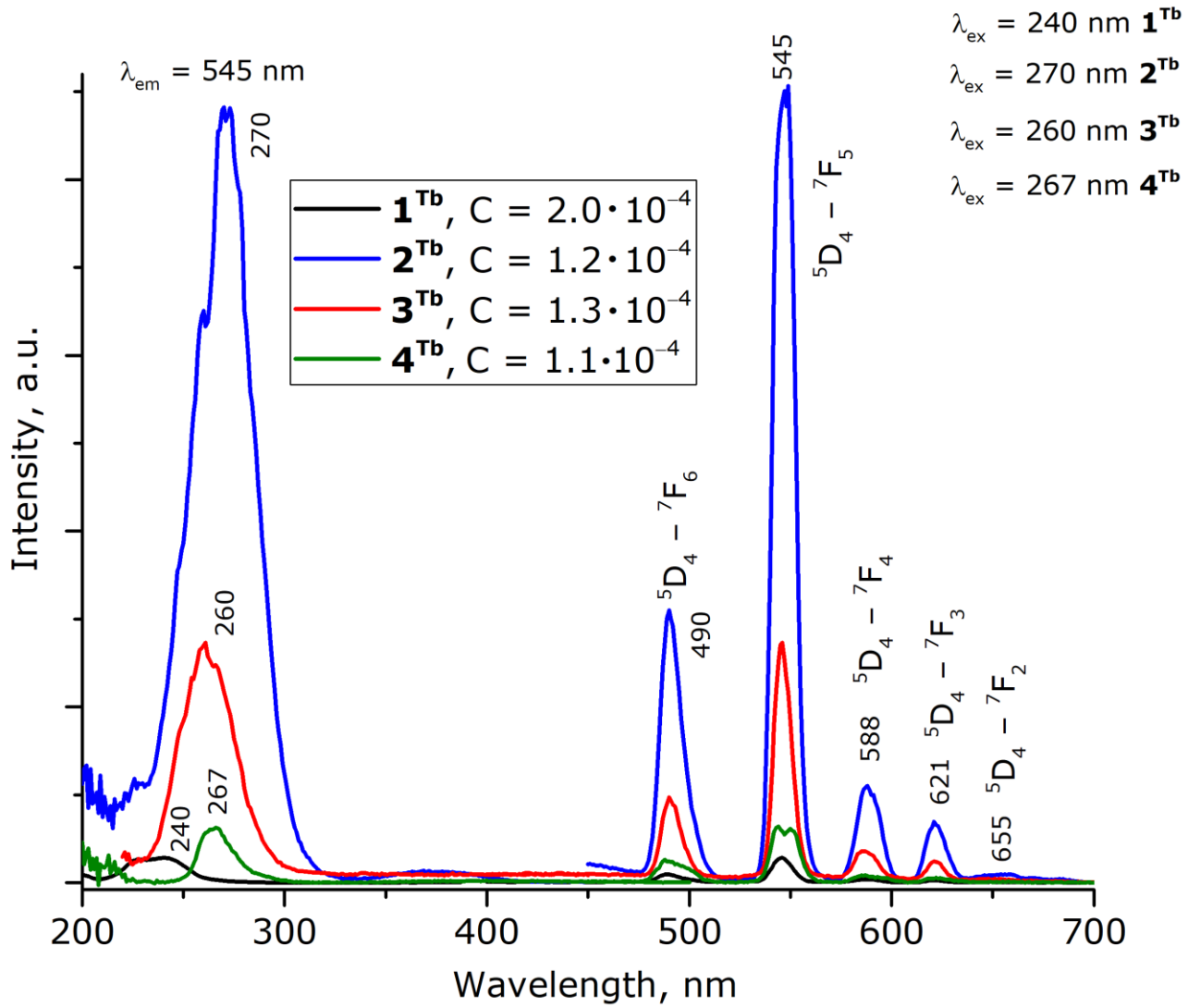

Fig. S9. Emission and excitation spectra of $\mathbf{1}^{Tb}$–$\mathbf{3}^{Tb}$ in thf solutions and $\mathbf{4}^{Tb}$ in CH_2Cl_2 solution. For all spectra 5 nm slit widths were used

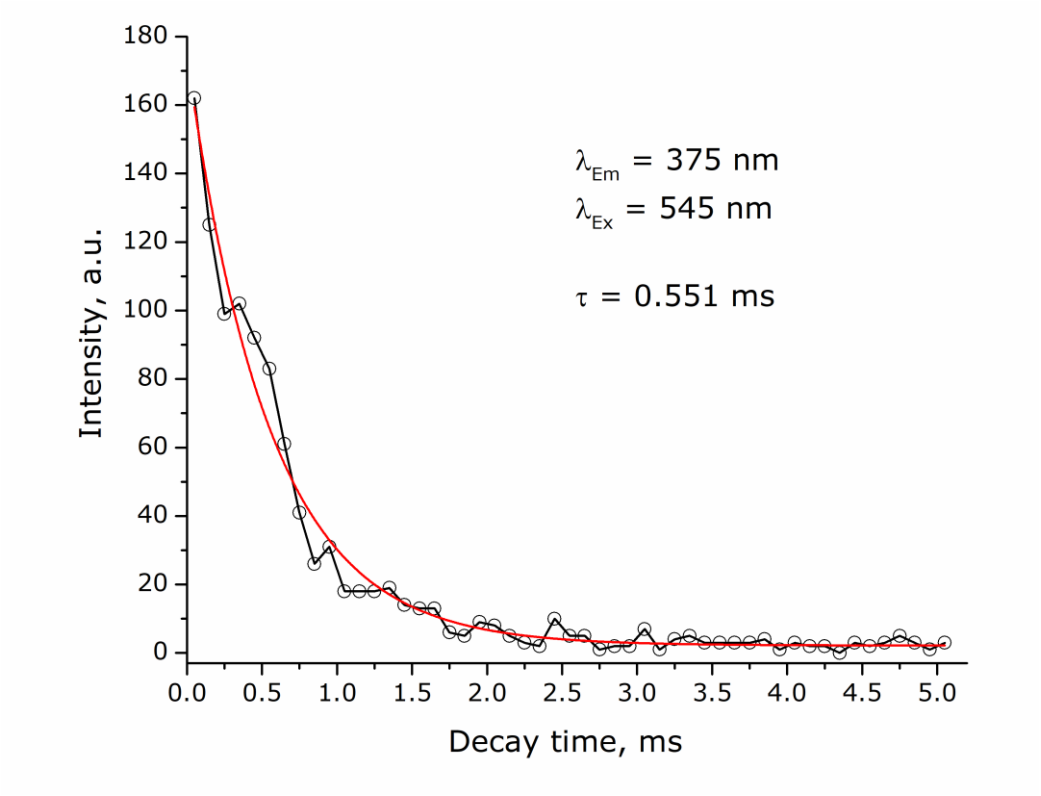

Fig. S10. Emission decay of solid-state luminescence of $\mathbf{1}^{\mathbf{Tb}}$ at 298 K

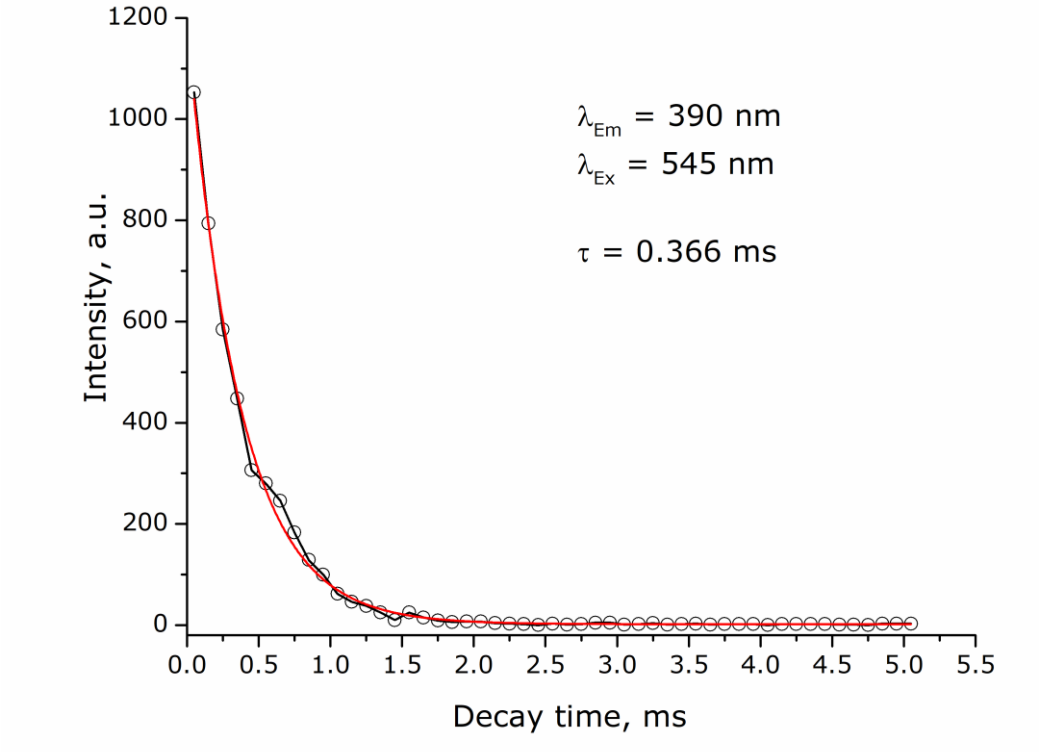

Fig. S11. Emisson decay of solid-state luminescence of $\mathbf{2}^{\mathbf{Tb}}$ at 298 K

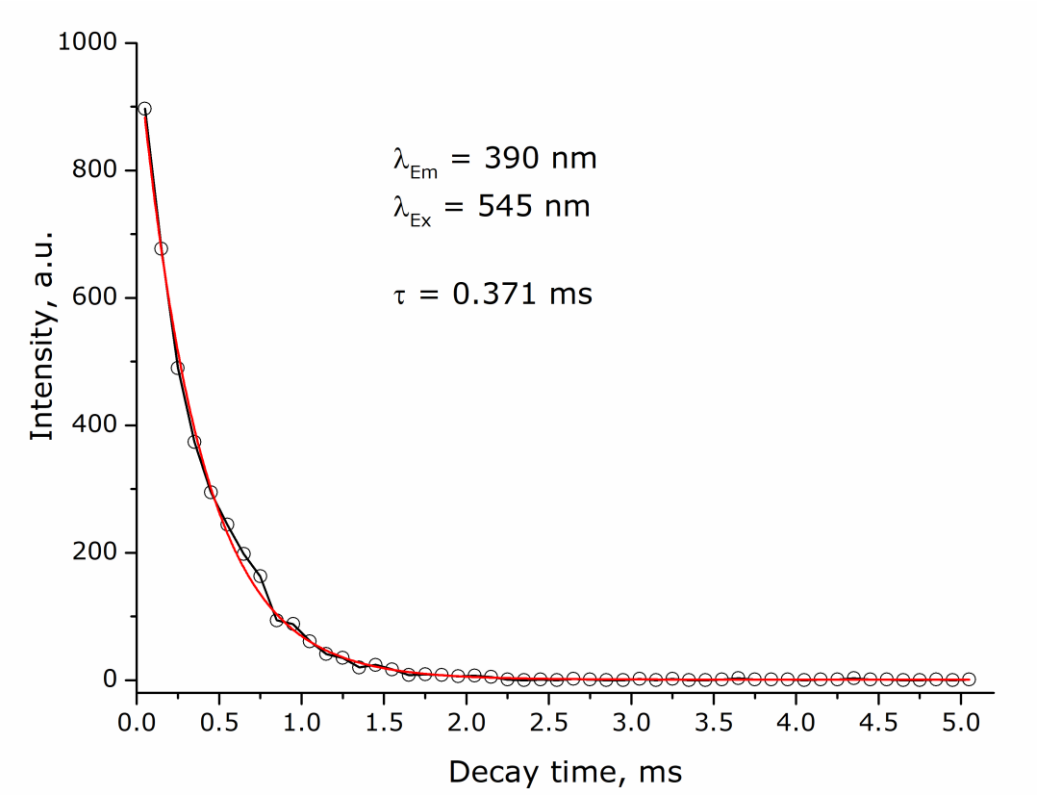

Fig. S12. Emission decay of solid-state luminescence of $\mathbf{3}^{\mathbf{Tb}}$ at 298 K

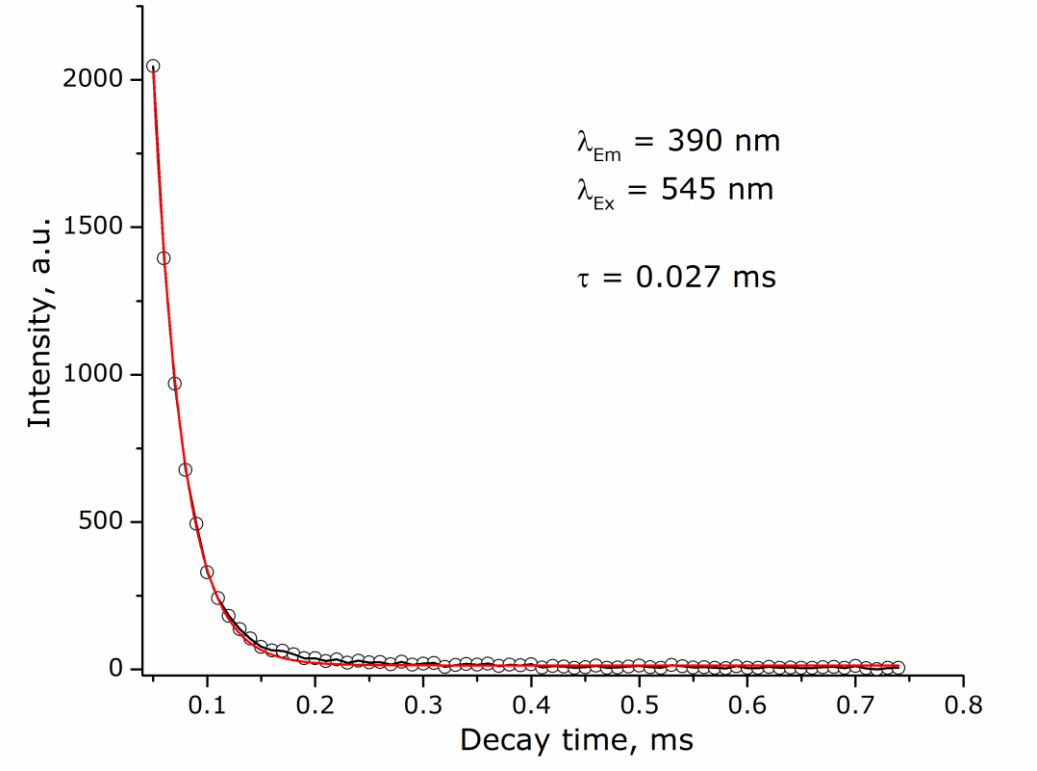

Fig. S13. Emission decay of solid-state luminescence of $\mathbf{4}^{\mathbf{Tb}}$ at 298 K

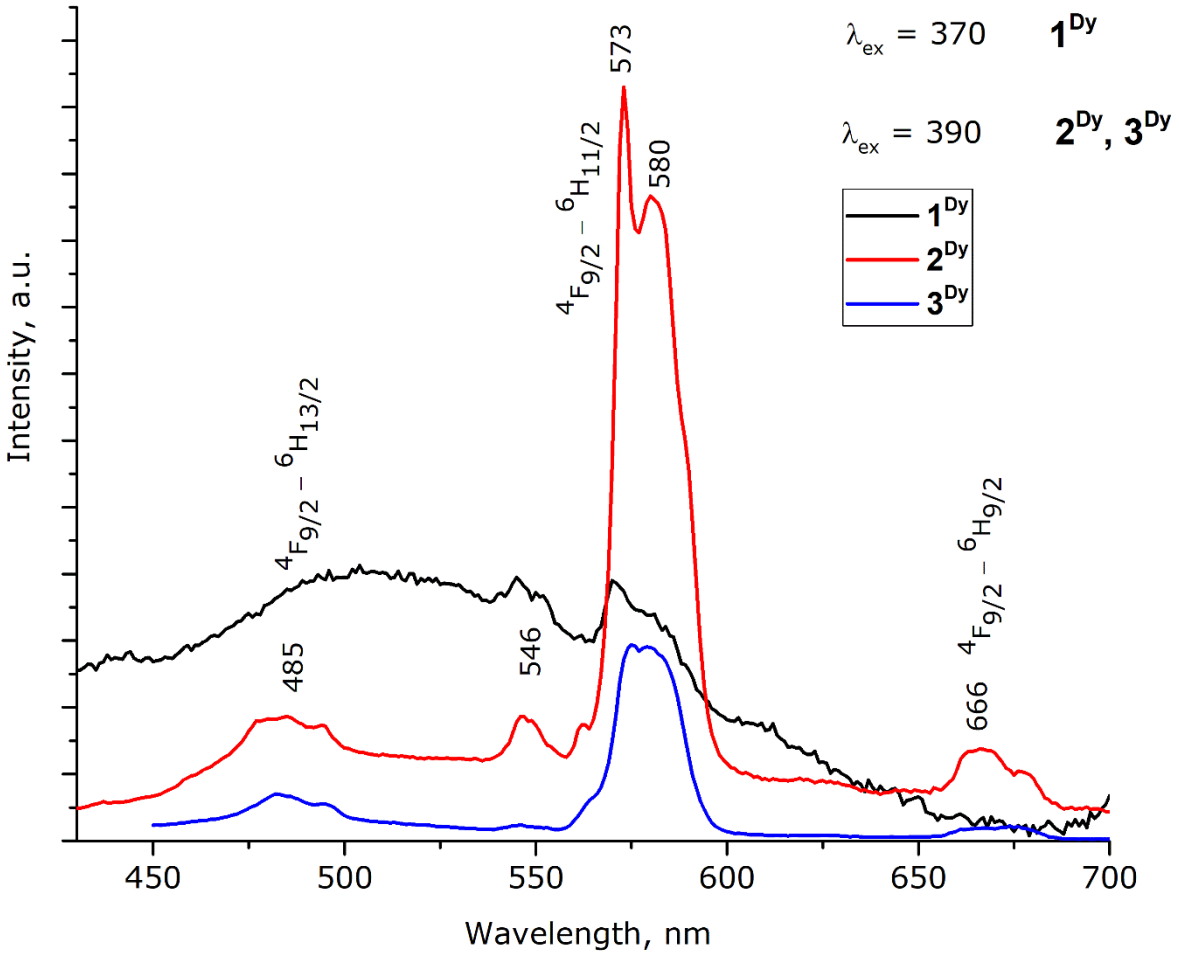

Figure S14. Emission spectra of $\mathbf{1}^{Dy}$, $\mathbf{2}^{Dy}$, and $\mathbf{3}^{Dy}$ solids (crystalline samples, room temperature, slit widths 3 , 3 and 5 nm, respectively)

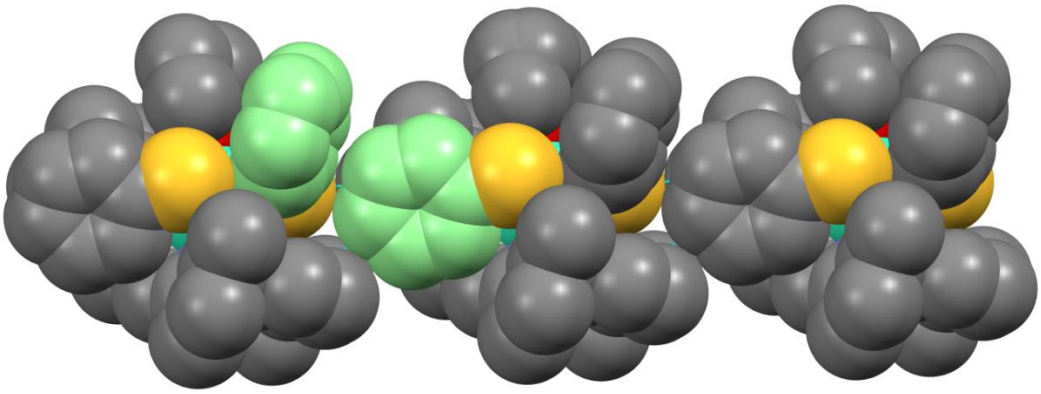

Figure S15. Packing of molecules of $\mathbf{2}^{\mathbf{Tb}}$ along the [100] direction in the crystal; three neighboring molecules are shown. A pair of the closest Ph cycles of the neighboring molecules are shown in green (edge-to-face type contact)

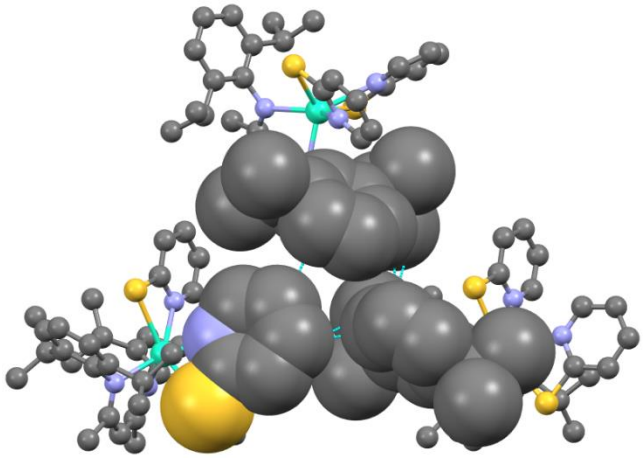

Figure S16. A group of three contacting molecules in the crystal of $\mathbf{3}^{\mathbf{Dy}}$·0.5thf (isostructural with the Tb complex). Only the closest SPy and Dipp moieties are shown in vdW spheres. The Py cycle has the closest contact with the top Dipp unit (shortest C···C distance of 3.7 Å)

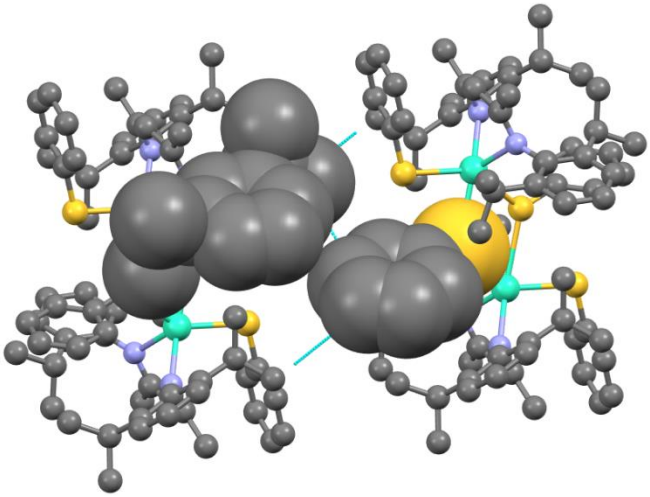

Figure S17. Packing interactions between μ-SPh and Dipp moieties of neighboring binuclear molecules in the structure of $\mathbf{4}^{\mathbf{Tb}}$·2toluene (shortest C···C distance of 3.4 Å). One of two symmetrical contacting pairs is shown in vdW spheres.