

Octahedral terbium(III) cationic bis(alkoxide) complexes: synthesis, structural features and luminescence

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General procedure

All operations were carried out under an argon atmosphere using Schlenk techniques or in a nitrogen-filled glovebox. After drying over KOH, THF and hexane were purified by distillation from sodium/benzophenone ketyl and stored under vacuum. $\text{Tb}(\text{o-CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_3$ was synthesized according to a literature procedure.^{S1} The fluorinated carbinols $\text{R}^1\text{R}^2\text{R}^3\text{COH}$ were purchased from SIA “P&M-Invest” Ltd. $(\text{C}_6\text{F}_5)_2\text{CHOH}$ and $\text{Ph}_2\text{C}(\text{CF}_2\text{Cl})\text{OH}$ were vacuumed for 8 h at room temperature and stored in a glovebox. $\text{CF}_3\text{C}(\text{Me})(\text{Ph})\text{OH}$ and $\text{Me}_2\text{C}(\text{C}_6\text{F}_5)\text{OH}$ were stirred under an inert atmosphere over CaH_2 for several days, condensed under vacuum, and stored in a glovebox. Lanthanide metal content was determined by complexometric titration.^{S2} Elemental analysis was performed in the Laboratory of Microanalysis, INEOS RAS. IR spectra were recorded as Nujol mulls using a Bruker Vertex-70 spectrophotometer.

X-Ray diffraction

Single crystals of the complexes were obtained by recrystallization from THF. Intensities of the reflections for all compounds were collected at Bruker Apex II CCD diffractometer ($\lambda(\text{Mo-K}\alpha) = 0.71073\text{\AA}$, ω -scans). The structures were solved by the SHELXT method^{S3} and refined by full-matrix least squares against F^2 . Non-hydrogen atoms were refined anisotropically, except those disordered. Two C_6F_5 groups and two THF molecules in **1**, a CF_2Cl group in **2**, all ligands in **3** and two THF molecules in **4** are equally disordered over two sites. Positions of hydrogen atoms were calculated and all of them were included in a refinement by the riding model with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_i)$ for methyl groups and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{ii})$ for other atoms. All calculations were made using the SHELXL2018/3^{S4} and OLEX2^{S5} program packages, the crystal data and refinement parameters are compiled in **Table S1**. Contribution of a disordered solvent molecule to reflection intensities in **1** was taken into account using “mask” procedure implemented to Olex2 package. CCBC 2497204 (**1**), 2497205 (**2**) 2497206 (**3**) 2497207 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/structures/>.

Photoluminescence measurements

Registration of luminescence spectra and excitation spectra in the solid phase, a Horiba Jobin-Yvon Fluorolog QM-75-22-C spectrofluorometer (HORIBA, Kyoto, Japan) with a 75 W xenon arc lamp (PowerArc, HORIBA, Kyoto, Japan) as a continuous excitation source was used. A Hamamatsu R13456 (Hamamatsu Photonics, Hamamatsu, Japan) cooled photomultiplier tube sensitive in UV-Vis-NIR region (200–950 nm) was used as the detector. Luminescence decays were recorded using the same setup and pulsed xenon lamp with a frequency of 100 Hz and a pulse duration of 50 μs . For cryogenic measurements, solid samples were placed in quartz capillaries and cooled to 77 K in a quartz cryostat filled with liquid nitrogen.

Synthesis of $[\text{o-Me}_2\text{NC}_6\text{H}_4\text{CH}_2]_2\text{Tb}[(\mu\text{-}\eta^4\text{:}\kappa^1\text{-Ph})\text{BPh}_3]$

To a solution of $\text{Tb}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})_3$ (1.50 g, 2.68 mmol) in 20 mL of toluene $[\text{HNEt}_3][\text{BPh}_4]$ (1.075 g, 2.55 mmol) was added at room temperature with vigorous stirring. After 20 minutes when colorless borate crystals dissolved, stirring was halted. In 8 h large dark-orange crystals of the product formed. The mother liquor was decanted and the crystals were washed with toluene and dried at ambient temperature under vacuum for 1 h. $[\text{Me}_2\text{NC}_6\text{H}_4\text{CH}_2\text{-o}]_2\text{Tb}[(\mu\text{-}\eta^4\text{:}\kappa^1\text{-Ph})\text{BPh}_3]$ was isolated in 65% yield (1.235 g). Elemental analysis calculated for $\text{C}_{42}\text{H}_{44}\text{BN}_2\text{Tb}$ (746.56 g/mol): C, 67.57; H, 5.94; N, 3.75; Tb, 21.29. Found: C, 67.24; H, 6.25; N, 3.99; Tb, 20.89. IR (Nujol, KBr) ν/cm^{-1} : 3058 (w), 3044(w), 3030 (w), 1591 (w), 1582 (w), 1429 (m), 1377 (m), 1299 (w), 1261 (m), 1207 (w), 1175 (w), 1158 (m), 1147 (w), 1102 (w), 1020 (w), 921 (m), 873 (m), 834 (m), 807 (m), 777 (m), 758 (s), 751 (w), 743 (w), 732 (s), 708 (s), 616 (w), 611 (m).

Synthesis of *cis*-[((C₆F₅)₂CHO)₂Tb(THF)₄][BPh₄] (**1**)

[*o*-Me₂NC₆H₄CH₂]₂Tb[(μ-η⁴:κ¹-Ph)BPh₃] (0.250 g, 0.33 mmol) was dissolved in 10 mL of THF, and a solution of (C₆F₅)₂CHOH (0.240 g, 0.66 mmol) in 5 mL of THF was added with vigorous stirring. The reaction mixture was stirred for 1 h, the volatiles were removed in vacuum, the remaining solid was dried, and then re-dissolved in a THF/hexane (2:1) mixture. Slow evaporation of the resulting solution at room temperature yielded colorless crystals of complex **1**. The mother liquor was decanted, and the crystals were washed with cold hexane and dried under vacuum. Complex **1** was isolated in 58% yield (0.285 g). Elemental analysis calculated for C₆₆H₅₄BF₂₀O₆Tb (1492,86 g/mol): C, 53,10; H, 3,65; Tb, 10,65. Found: C, 52,81; H, 3,39; Tb, 10,34. IR (Nujol, KBr) ν/ cm⁻¹: 1652 (w), 1580 (w), 1305 (m), 1261 (w), 1181 (m), 1157 (m), 1135 (m), 1121 (m), 1004 (s), 962 (w), 909 (w), 858 (w), 818 (w), 733 (m), 706 (m).

Synthesis of *cis*-[(Ph)₂(CF₂Cl)CO)₂Tb(THF)₄][BPh₄] (**2**)

A procedure similar to that for the synthesis of **1** was employed using Ph₂C(CF₂Cl)OH (0.177 g, 0.66 mmol). Complex **2** was isolated in 57% yield (0.244 g). Elemental analysis calculated for C₆₈H₇₂BCl₂F₄O₆Tb (1301,95 g/mol): C, 62,73; H, 5,57; Tb, 12,21. Found: C, 62,39; H, 5,24; Tb, 11,98. IR (Nujol, KBr) ν/ cm⁻¹: 1636 (w), 1591 (w), 1310 (m), 1176 (w), 1156 (m), 1135 (w), 1119 (m), 999 (s), 954 (w), 875 (w), 818 (w), 734 (m).

Synthesis of *cis*-[(Ph)(Me)(CF₃)CO)₂Tb(THF)₄][BPh₄] (**3**)

A procedure similar to that for the synthesis of **1** was employed using CF₃C(Me)(Ph)OH (0.126 g, 0.66 mmol). Complex **3** was isolated in 49% yield (0.185 g). Elemental analysis calculated for C₅₈H₆₈BF₆O₆Tb (1144,90 g/mol): C, 60,85; H, 5,99; Tb, 13,88. Found: C, 60,53; H, 5,68; Tb, 14,02. IR (Nujol, KBr) ν/ cm⁻¹: 1579 (w), 1462 (s), 1377 (s), 1281 (m), 1234 (m), 1150 (s), 1096 (m), 1067 (m), 1030 (w), 1011 (m), 968 (w), 917 (w), 861 (m), 766 (w), 734 (s), 708 (s), 659 (w), 638 (w), 613 (w).

Synthesis of *cis*-[(C₆F₅)(Me)₂CO)₂Tb(THF)₄][BPh₄] (**4**)

A procedure similar to that for the synthesis of **1** was employed using Me₂C(C₆F₅)OH (0.149 g, 0.66 mmol). Complex **4** was isolated in 55% yield (0.221 g). Elemental analysis calculated for C₅₈H₆₄BF₁₀O₆Tb (1216,86 g/mol): C, 57,25; H, 5,30; Tb, 13,06. Found: C, 56,90; H, 5,05; Tb, 13,41. IR (Nujol, KBr) ν/ cm⁻¹: 1581 (w), 1440 (s), 1380 (s), 1285 (m), 1214 (m), 1101 (s), 1089 (m), 1067 (m), 935 (w), 866 (m), 764 (w), 738 (s), 712 (s), 643 (w).

IR spectra

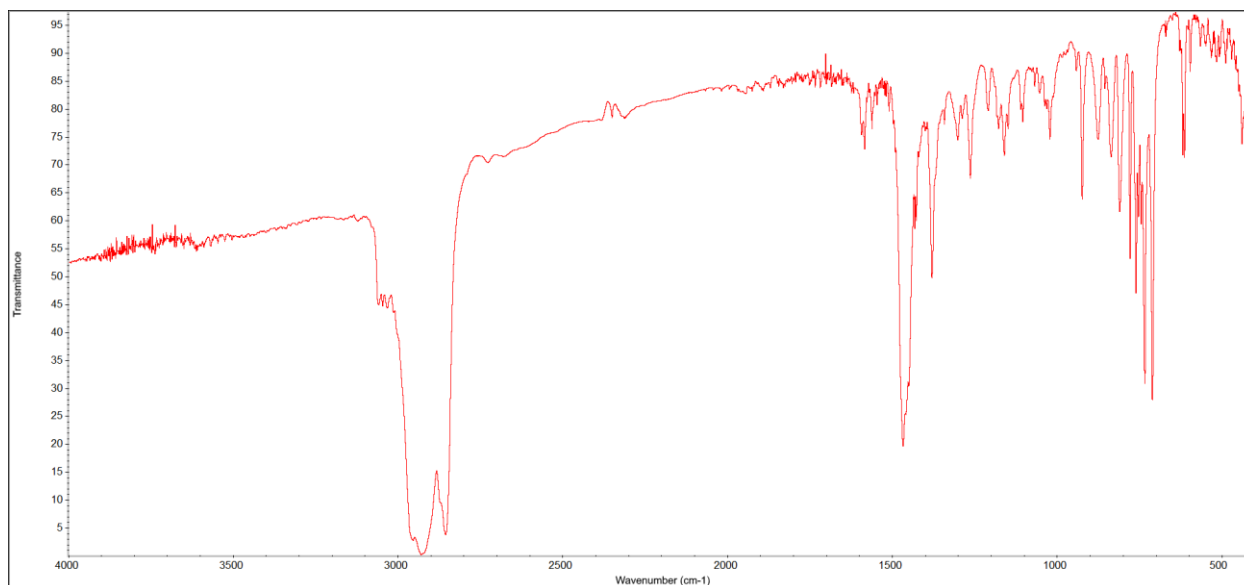


Figure S1. IR spectrum of [*o*-Me₂NC₆H₄CH₂]₂Tb[(μ₂-η⁴:κ¹-Ph)BPh₃] (Nujol, KBr).

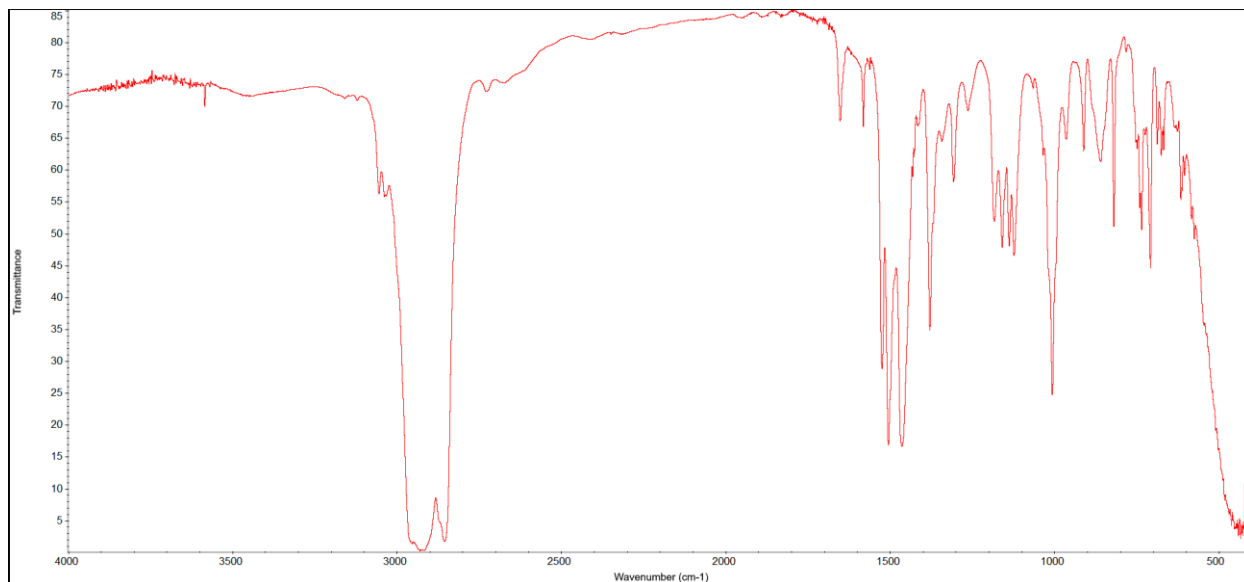


Figure S2. IR spectrum of **1** (Nujol, KBr).

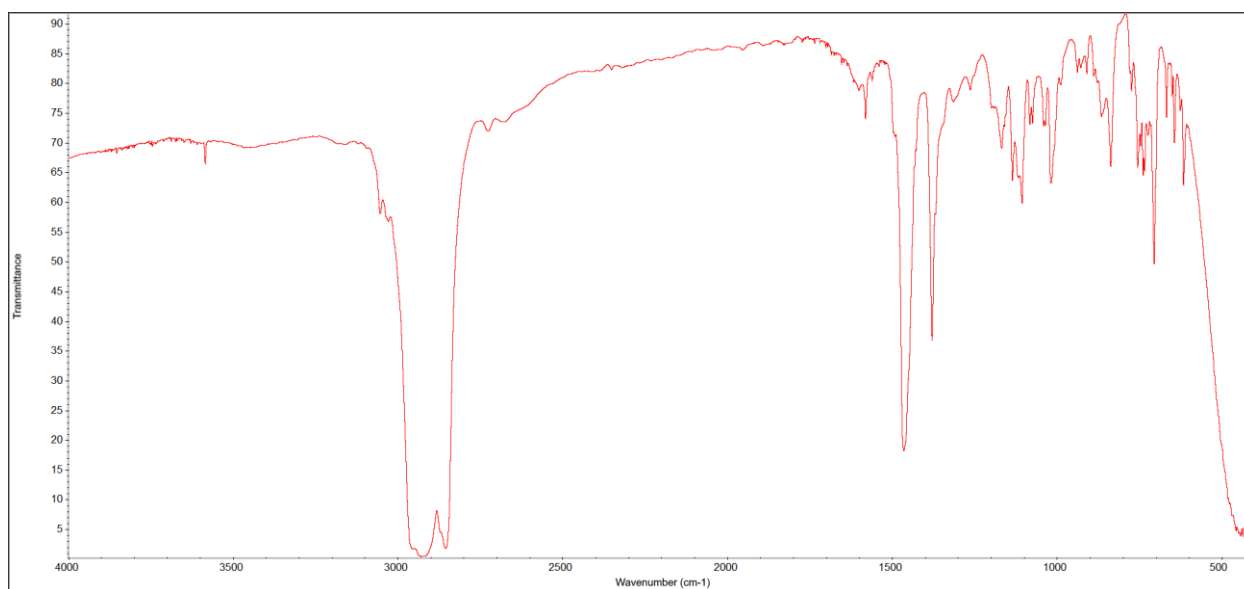


Figure S3. IR spectrum of **2** (Nujol, KBr).

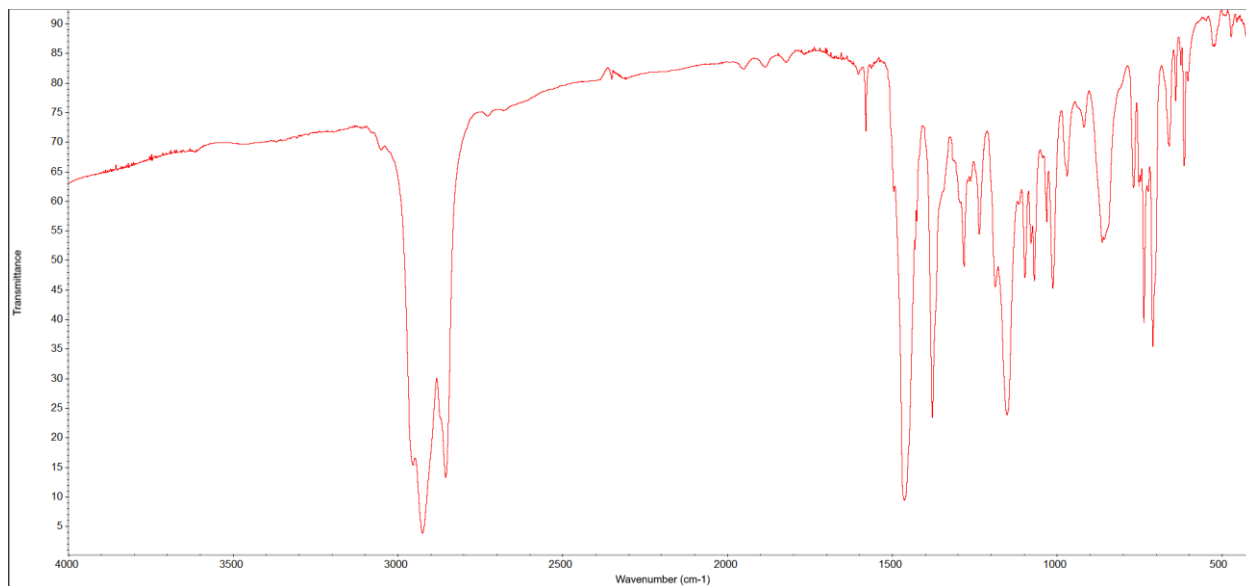


Figure S4. IR spectrum of **3** (Nujol, KBr).

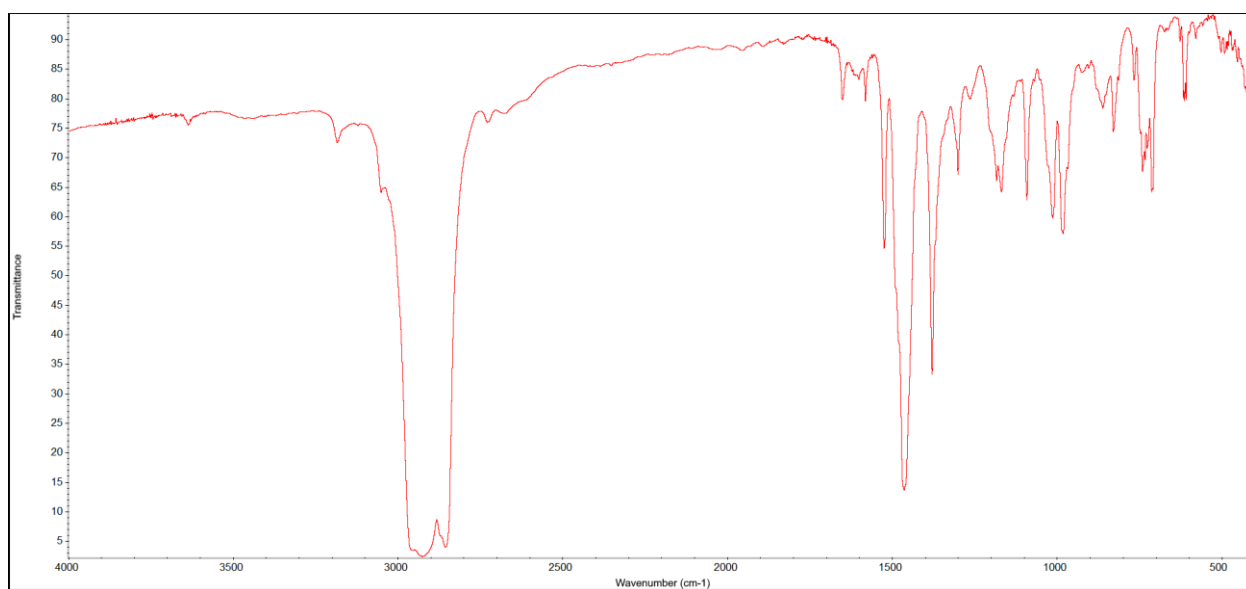


Figure S5. IR spectrum of **4** (Nujol, KBr).

Luminescence

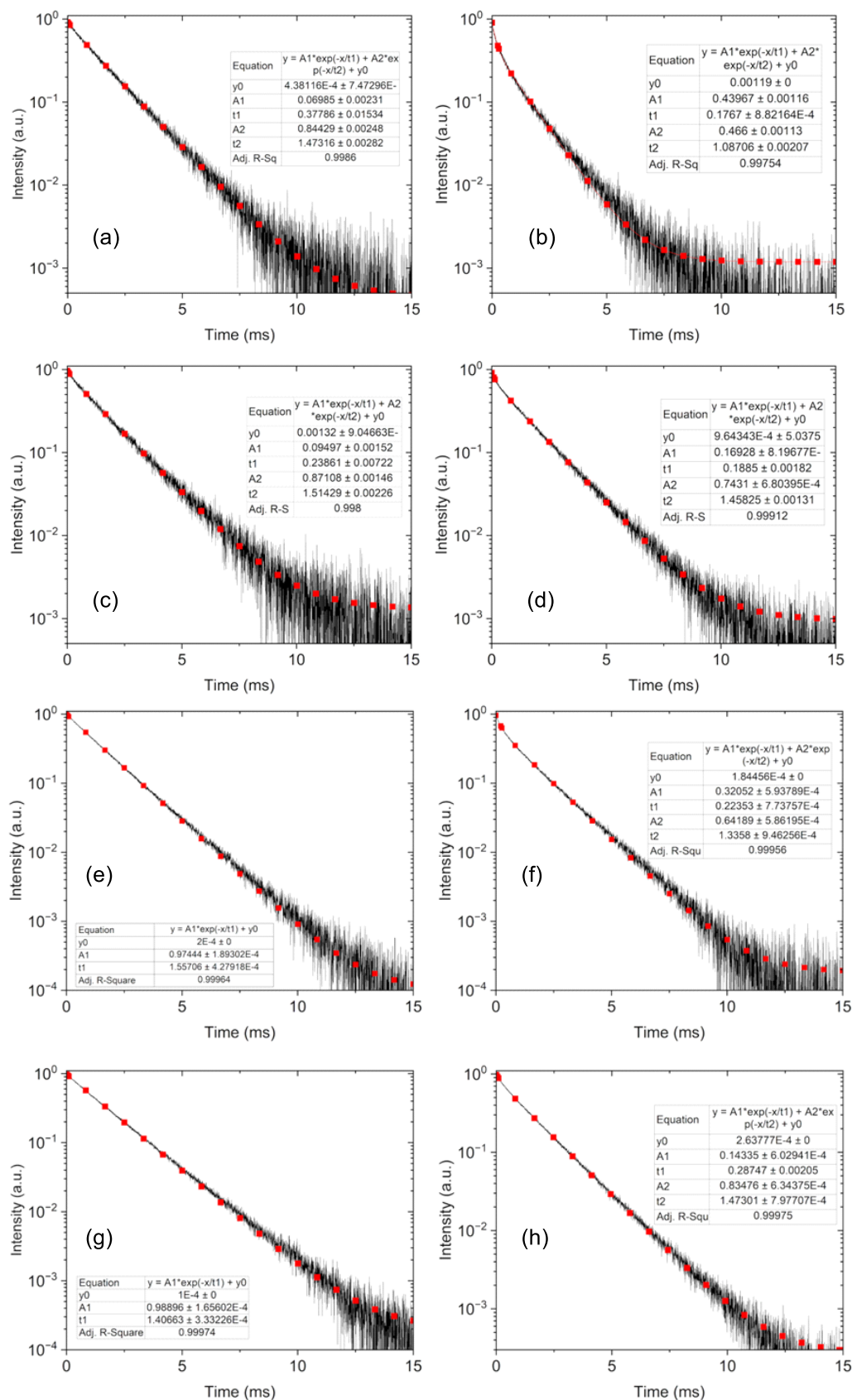


Figure S6. The luminescence decay profiles of (a),(e) complex 1, (b),(f) complex 2, (c),(g) complex 3 and (d),(h) complex 4 recorded at (a)–(d) 77 K and (e)–(h) 300 K.

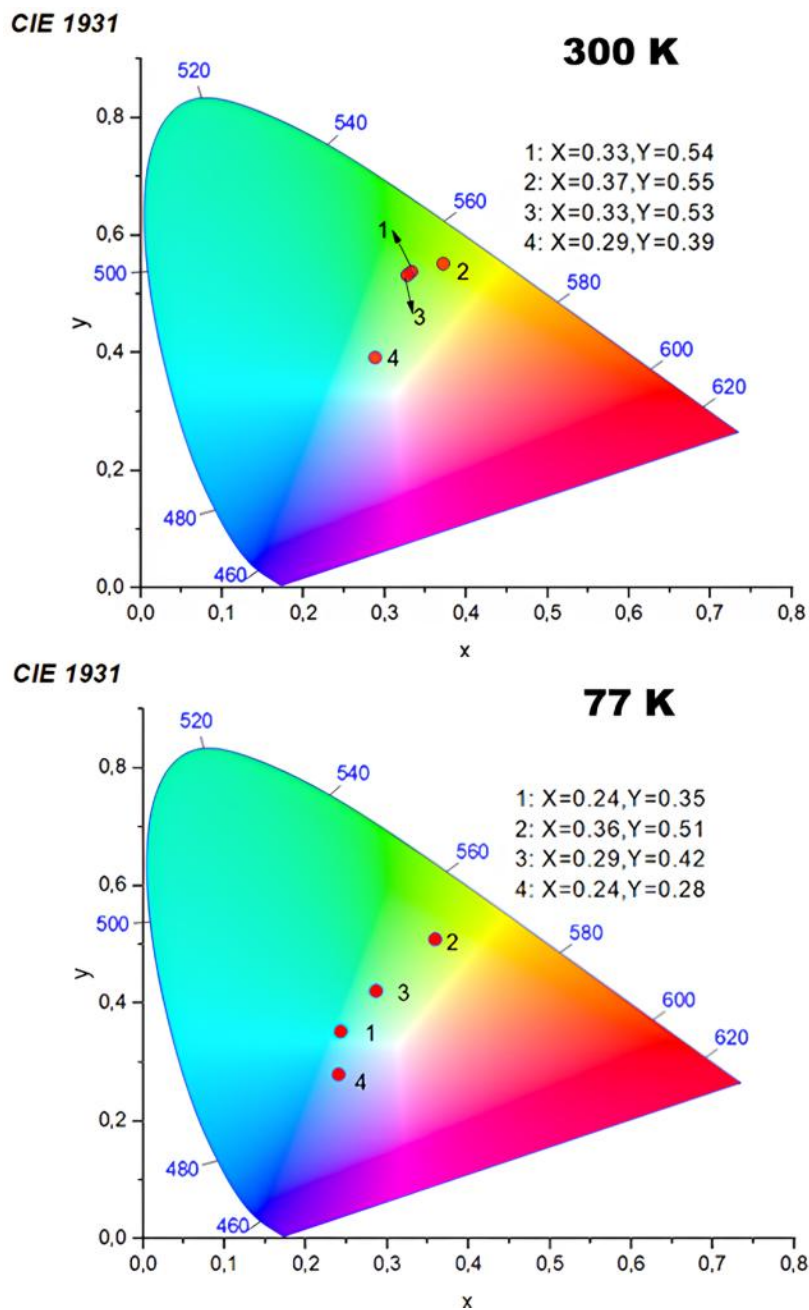


Figure S7. CIE color diagram of luminescence for the complexes **1-4**.

Table S1. Luminescence lifetimes of complexes **1-4**.

Complex	300 K		77 K	
	t_1/ms	t_2/ms	t_1/ms	t_2/ms
1	-	1.56	0.38	1.47
2	0.22	1.34	0.18	1.09
3	-	1.41	0.24	1.51
4	0.29	1.47	0.19	1.46

Crystallographic data

Table S2. Crystal data, data collection and structure refinement details for studied compounds.

	1 ·[THF]	2	3	4
Formula	C ₇₀ H ₆₂ BF ₂₀ O ₇ Tb	C ₆₈ H ₇₂ BCl ₂ F ₄ O ₆ Tb	C ₅₈ H ₆₈ BF ₆ O ₆ Tb	C ₅₈ H ₆₄ BF ₁₀ O ₆ Tb
<i>M</i>	1564.92	1301.88	1144.923	1216.885
<i>T</i> , K	120	120	120	120
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁ /c	P2 ₁ /n	P2 ₁ /n	P-1
<i>Z</i> (<i>Z'</i>)	4 (1)	4 (1)	4 (1)	2 (1)
<i>a</i> , Å	20.9867(15)	21.1219(4)	19.493(3)	10.7867(5)
<i>b</i> , Å	12.6014(10)	13.4178(3)	13.861(2)	12.2901(6)
<i>c</i> , Å	26.1380(19)	21.7051(4)	21.167(3)	21.0139(10)
α , deg	90	90	90	83.399(2)
β , deg	106.054(3)	102.306(1)	111.312(4)	8.246(2)
γ , deg	90	90	90	75.440(2)
<i>V</i> , Å ³	6642.9(9)	6010.1(2)	5328.1(14)	2678.5(2)
<i>d</i> _{calcd} , g·cm ⁻³	1.565	1.439	1.427	1.509
μ , mm ⁻¹	11.75	13.30	13.98	14.06
<i>F</i> ₀₀₀	3152	2680	2352	1240
2 θ _{max} , deg	52	61	56	62
Number of measured refl.	72336	65751	64805	37174
Number of independent refl. (<i>R</i> _{int})	20466 (0.106)	18338	12876	16876
Observed refl. [<i>I</i> > 2 σ (<i>I</i>)]	12941	14146	6290	15086
Parameters	956	745	584	681
<i>R</i> ₁ [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.1324	0.0357	0.0827	0.0285
<i>wR</i> ₂ (all data)	0.3000	0.0939	0.2016	0.0686
<i>S</i> (<i>F</i> ²)	0.989	1.017	1.111	0.977
Residual density (<i>d</i> _{max} / <i>d</i> _{min}), e·Å ⁻³	4.044/-4.461	3.977/-1.866	1.059/-0.938	1.694/-1.378

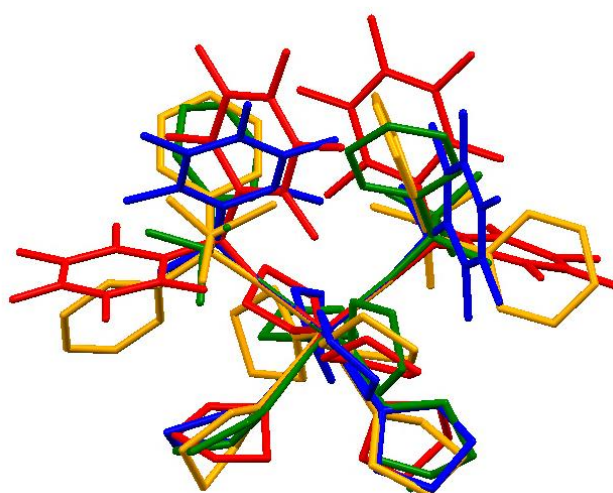
Table S3. SHAPE analysis for **1** - **4**.^a

	1	2	3	4
OC-6	0.667	0.620	0.409	0.513
TRP-6	15.345	15.271	15.270	15.671
PPY-6	26.846	27.776	28.165	28.234
JPPY-6	30.201	31.185	31.595	31.540
HP-6	31.836	31.888	33.062	31.614

^a The sum of atomic deviations (Å) from an ideal octahedron (OC-6), trigonal prism (TRP-6), pentagonal pyramid (PPY-7), Johnson pentagonal pyramid (JPPY-6) or hexagon (HP-6) geometry obtained using the Shape program.^{S6}

Table S4. Some relevant crystallographic parameters for **1–4**.

Complex	Bond angle (THF ^{apical})O-Tb- O(THF ^{apical})/°	Bond angle O- Tb-O /°	Tb-O bond lengths/Å	Tb-O(THF ^{apical}) bond lengths/Å	Tb-O(THF ^{equatorial}) bond lengths/Å
1	162.7(4)	107.2(4)	2.091(10), 2.08(1)	2.371(12), 2.364(11),	2.437(10), 2.411(10)
2	163.86(5)	106.68(6)	2.1047(15), 2.0945(14)	2.3866(14), 2.3821(15)	2.4525(15), 2.4500(14)
3	165.8(2)	104.4(2)	2.076(6)	2.364(6), 2.359(6)	2.432(7), 2.427(6)
4	169.22(5)	105.01(5)	2.0880(13), 2.0749(13)	2.3961(13), 2.3789(13)	2.4524(14), 2.4301(14)

**Figure S8.** Molecular conformations of the cationic complexes **1** (red), **2** (orange), **3** (green) and **4** (blue) with overlaid Tb and OCR¹R²R^F atoms. Hydrogen atoms and the [BPh₄][−] moieties have been omitted for clarity.

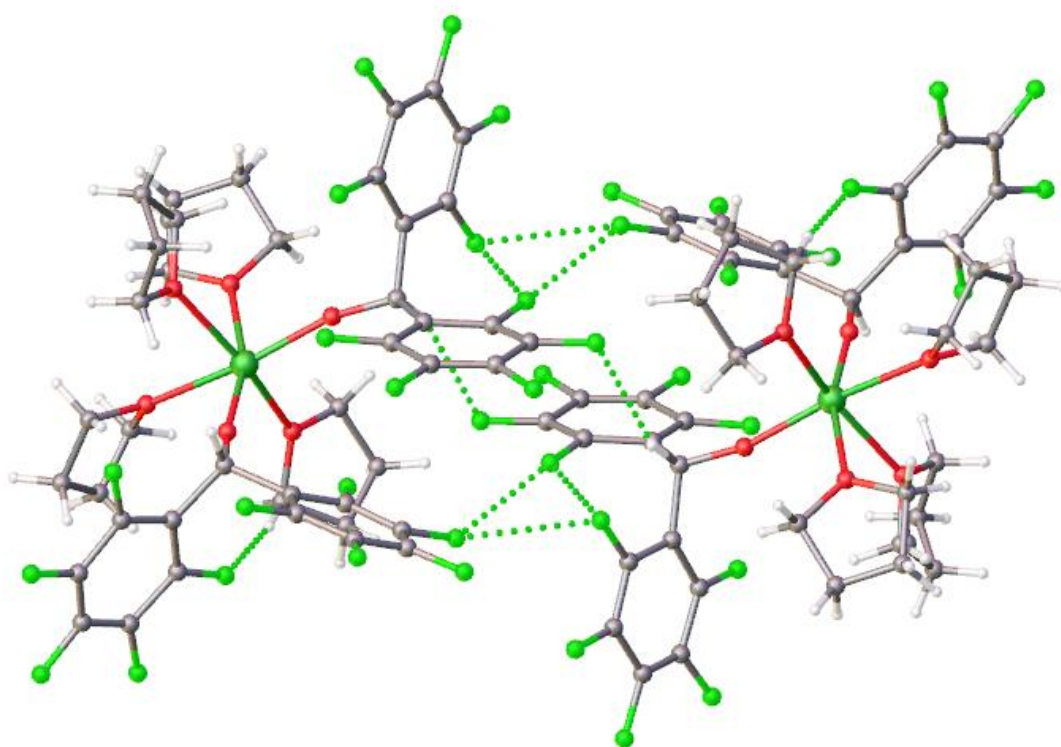


Figure S9. A dimer of cations in **1** formed by F...F ($r(\text{F}\cdots\text{F}) = 2.56(3) - 3.30(4) \text{ \AA}$) and C-H...F interactions.

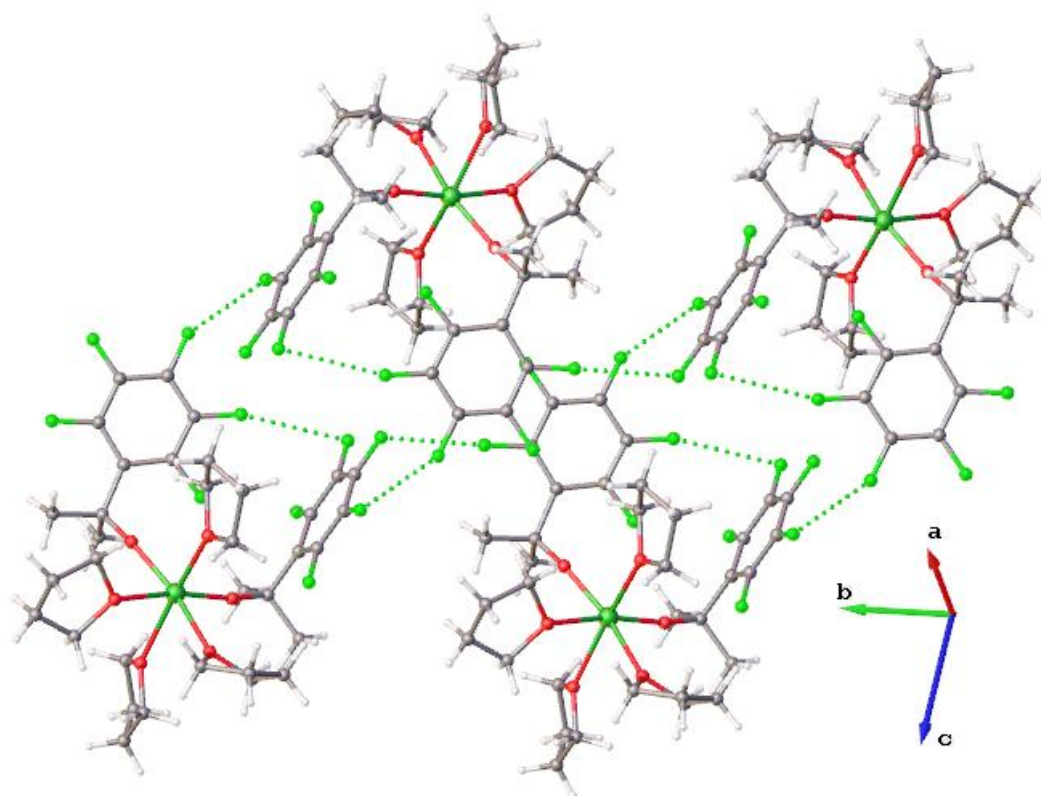


Figure S10. A chain of cations in **4** formed by F...F ($r(\text{F}\cdots\text{F}) = 2.907(2) - 3.193(2) \text{ \AA}$) and C-H...F interactions.

References

- S1 D. M. Kuzyaev, T. V. Balashova, M. E. Burin, G. K. Fukin, R. V. Rumyantsev, A. P. Pushkarev, V. A. Ilichev, I. D. Grishin, D. L. Vorozhtsov and M. N. Bochkarev, *Dalton Trans.*, 2016, **45**, 3464; <https://doi.org/10.1039/C5DT04636J>.
- S2 J. Goura, J. Brambleby, C. V. Topping, P. A. Goddard, R. Suriya Narayanan, A. K. Bar and V. Chandrasekhar, *Dalton Trans.*, 2016, **45**, 9235; <https://doi.org/10.1039/C5DT03871E>.
- S3 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3; <https://doi.org/10.1107/S2053229614024218>.
- S4 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3; <https://doi.org/10.1107/S2053273314026370>.
- S5 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339; <https://doi.org/10.1107/S0021889808042726>.
- S6 S. Alvarez, D. Avnir, M. Llunell and M. Pinsky, *New J. Chem.*, 2002, **26**, 996; <https://doi.org/10.1039/b200641n>.