Supporting Information

Metalloid germanium cluster shears for lanthanide diiodides

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Experimental Procedures

General Considerations

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line, or in an argon-filled glove box. Elemental analyses were carried out with an Elementar vario MICRO Cube. Tetrahydrofuran was distilled under nitrogen from sodium benzophenoneketyl and degassed before storage over Na/K alloy. *n*-Hexane was distilled under nitrogen from sodium, degassed and stored in vacuo over Na/K alloy. $(thf)_2SmI_2$[1,2], $(thf)_2EuI_2$[2], $(thf)_2YbI_2$[2] and $K[Ge_9(Hyp)_3]$[3] were prepared according to literature procedures.
NMR spectroscopic measurements were performed by using a Bruker AVIIIHD-300 spectrometer. The chemical shifts are given in ppm against the external standard $SiMe_4$. THF-d_8 was dried with Na/K alloy and stored in a glove box under an argon atmosphere. The INEPT pulse program was used for the ^{29}Si NMR spectroscopic experiments.
UV/Vis measurements were performed using a PG Instruments T60 UV/visible spectrophotometer in the quartz cuvette 1 mm thick.

X-ray diffraction analysis

Crystals were mounted on the diffractometer at 150 K (**1**), 200 K (**2**) or 100 K (**3**). The data were collected either on a Bruker APEX II DUO diffractometer equipped with an IμS microfocus sealed tube and QUAZAR optics for monochromated MoKα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems cryostat or on a Rigaku XtaLAB Synergy-S X-ray diffractometer for single crystal X-ray diffraction equipped with a PhotonJet-S microfocus sealed tube for monochromated MoKα radiation. An absorption correction was applied using the programs SADABS and CrysAlisPro. The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs used: SHELXT and SHELXL[4] within the Olex2 program package.[5]
The compounds **2** and **3** cannot be refined properly in the orthorhombic crystal system, although the monoclinic angle is with 90.14° quite similar to 90°. This, and the fact of having problems with finding single crystals without any second domain, leads us to a refinement with lower symmetry (monoclinic instead of orthorhombic) with the twin law: 1 0 0 0 -1 0 0 0 -1 and a scaling factor of 0.37 (for **3**), or being lucky with a refinement of two domains using HKLF5 (scaling factor 0.37) for **2**.The cations in **2** and **3** are refined as split positions indicated by the special position on an inversion centre. Also a second splitting of the four-membered Ln_2I_2 ring in **2** and **3** are necessary to get good R values.
The H atom positions in all compounds were refined using a riding model. The supplementary crystallographic data (for CCDC 2241576 (**1**), 2241575 (**2**) and 2241577 (**3**)) can be obtained online free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

Luminescence measurements

Steady-state spectra of THF solutions of **2**, EuI_2 and $[(thf)_2Eu(Ge_9(Hyp)_3)_2]$ (in the NMR-tube under argon) were measured on a Horiba Fluorolog-3 spectrofluorimeter equipped with a 450 W xenon lamp for steady-state measurements. For time-gated spectra and phosphorescence lifetime measurements, excitation was performed with a pulsed xenon lamp (pulse width ca. 2 µs FWHM) using the excitation monochromator pathway. Emitted light was detected by a Hamamatsu R2658P PMT (UV/vis/NIR, 200 nm < λ_{em} < 1000 nm) detector. A double grating monochromator 320DFX (1200 grooves/nm, blazed at 330 nm) was used for spectral selection in the excitation path, while in the emission path the single grating monochromator iHR550 (1200 grooves/nm, blazed at 500 nm) was used. To avoid higher order excitation light, long pass filter glass plates were used when needed.
Lifetime data analysis (deconvolution, statistical parameters, etc.) was performed using the software DAS analysis from Horiba. The decay data were analysed by reconvolution fitting with the instrument response function (IRF), which was determined using a dilute aqueous dispersion of colloidal silica (Ludox® AM-30).

Magnetic measurements

Magnetic data on microcrystalline samples were collected with a Quantum Design MPMS 3. DC susceptibility data were collected on samples restrained within a polycarbonate gel capsule. Variable-temperature measurements were performed at the applied magnetic field of 0.1 or 1 T with 1 K min^{-1} heating rate and 5 K intervals. Magnetic susceptibility data were corrected for sample holder and underlying diamagnetism by using an estimation $\chi_{m,diamag} = 1/2\ M_w \bullet 10^{-6}$ cm^3 mol^{-1}, with M_w being the molar mass of the complex.[6] The fits were performed using the program PHI version 3.1.5.[7]

Synthesis of $[(thf)_4YbI]_2[\eta^1\text{-}Ge_9(Hyp)_3]_2$ (1) and $[(thf)_5LnI]_4[\eta^2,\eta^3\text{-}Ge_9(Hyp)_3]_4$ (Ln = Eu (2), Sm (3))

$(thf)_2LnI_2$ (1 equiv.) and $K[Ge_9(Hyp)_3]$ (1 equiv.) were stirred in THF (20 mL) for 24 h at ambient temperature. Then THF was removed by evaporation in vacuum and *n*-hexane (20 mL) was condensed. The suspension was stirred for another 24 h and *n*-hexane was evaporated to dryness. The residue was dissolved in THF (10 mL). After two days the precipitated potassium iodide was filtered off. Then the solution was concentrated to 5 mL and carefully layered with *n*-hexane (15 mL). The long needle-shaped orange crystals of **1** and **2** and dark-brown crystals of **3** were grown within a week, washed with *n*-hexane, a little dried in vacuum and collected in the glove box with the moderate yields.
1 (from 86 mg (0.15 mmol) of $(thf)_2YbI_2$ and 215 mg (0.15 mmol) of $K[Ge_9(Hyp)_3]$): Orange crystals, 135 mg (0.068 mmol, 45%). Anal. calcd (%) for $C_{43}H_{113}Ge_9IO_4Si_{12}Yb$ (1984.66): C 26.02, H 5.74. Found C 25.84, H 5.71. ^1H NMR (THF-d_8, 300 MHz): δ = 0.25 (s, 81 H, $Si(SiMe_3)_3$), 1.77 (m, 16 H, THF), 3.62 (m, 16 H, THF) ppm; $^{13}C\{^1H\}$ NMR (THF-d_8, 75 MHz): δ = 3.0 ($Si(SiMe_3)_3$), 26.2 (THF), 68.0 (THF) ppm; ^{29}Si-inept-NMR (THF-d_8, 119.2 MHz): δ = -9.8 (-$Si(\mathit{Si}Me_3)_3$), -108.1 (-$\mathit{Si}(SiMe_3)_3$) ppm.

2 (from 83 mg (0.15 mmol) of $(thf)_2EuI_2$ and 215 mg (0.15 mmol) of $K[Ge_9(Hyp)_3]$): Orange crystals, 85 mg (0.042 mmol; 28%). Anal. calcd (%) for $C_{47}H_{121}Ge_9IO_5Si_{12}Eu$ (2036.07): C 27.73, H 5.99. Found C 27.59, H 5.88.

3 (from 82 mg (0.15 mmol) of $(thf)_2SmI_2$ and 215 mg (0.15 mmol) of $K[Ge_9(Hyp)_3]$): Dark-green crystals, 117 mg (0. 058 mmol; 38%). Anal. calcd (%) for $C_{47}H_{121}Ge_9IO_5Si_{12}Sm$ (2034.47): C 27.75, H 6.00. Found C 27.54, H 5.82. ^1H NMR (THF-d_8, 300 MHz): δ = 0.27 (s, 81 H, $Si(SiMe_3)_3$), 1.78 (m, 15 H, THF), 3.62 (m, 15 H, THF) ppm; $^{13}C\{^1H\}$ NMR (THF-d_8, 75 MHz): δ = 2.8 ($Si(SiMe_3)_3$), 26.0 (THF), 68.0 (THF) ppm; ^{29}Si-inept-NMR (THF-d_8, 119.2 MHz): δ = -9.8 ($-Si(\mathit{Si}Me_3)_3$), -108.2 ($-\mathit{Si}(SiMe_3)_3$) ppm.

UV/Vis spectroscopy

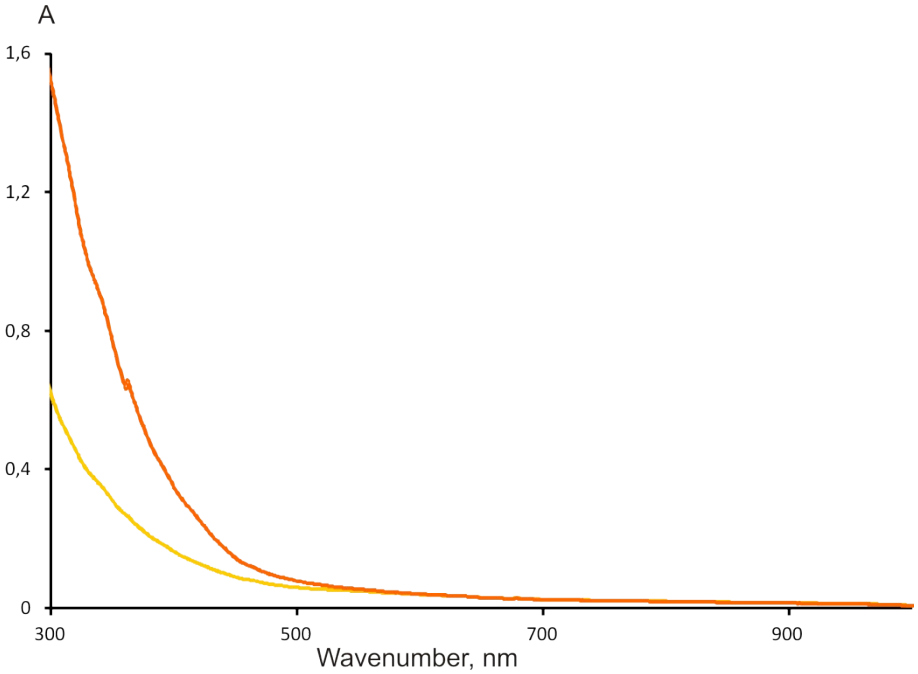

Fig. S1 The UV-Vis spectrum of **1** recorded in THF at room temperature.

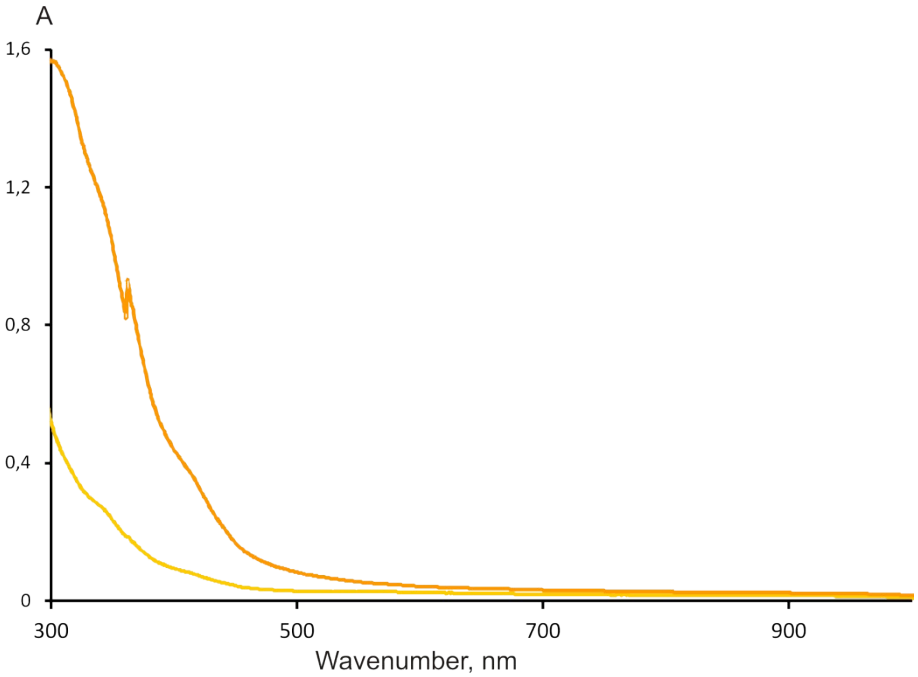

Fig. S2 The UV-Vis spectrum of **2** recorded in THF at room temperature.

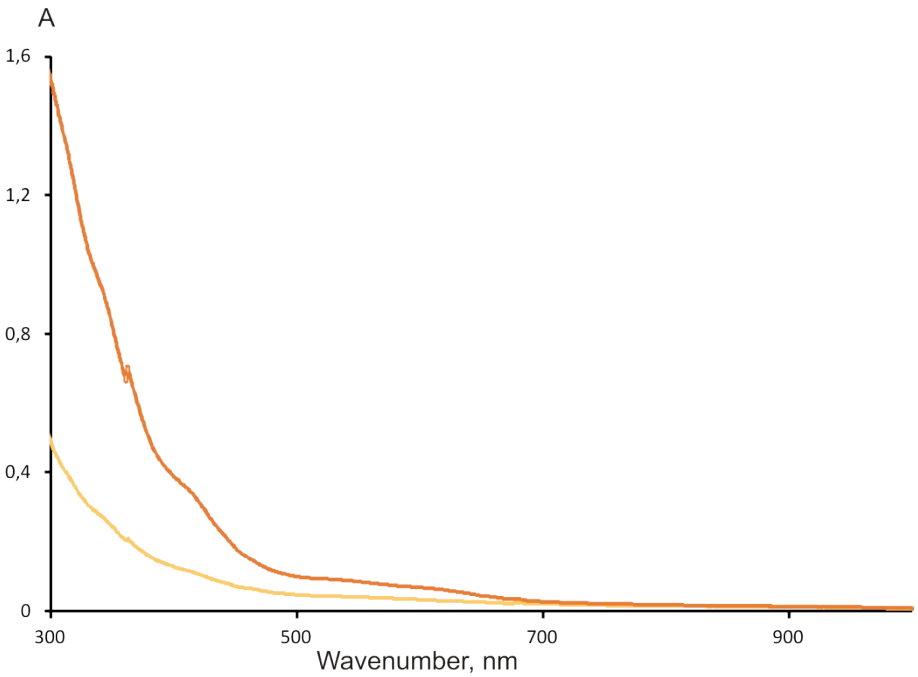

Fig. S3 The UV-Vis spectrum of **3** recorded in THF at room temperature.

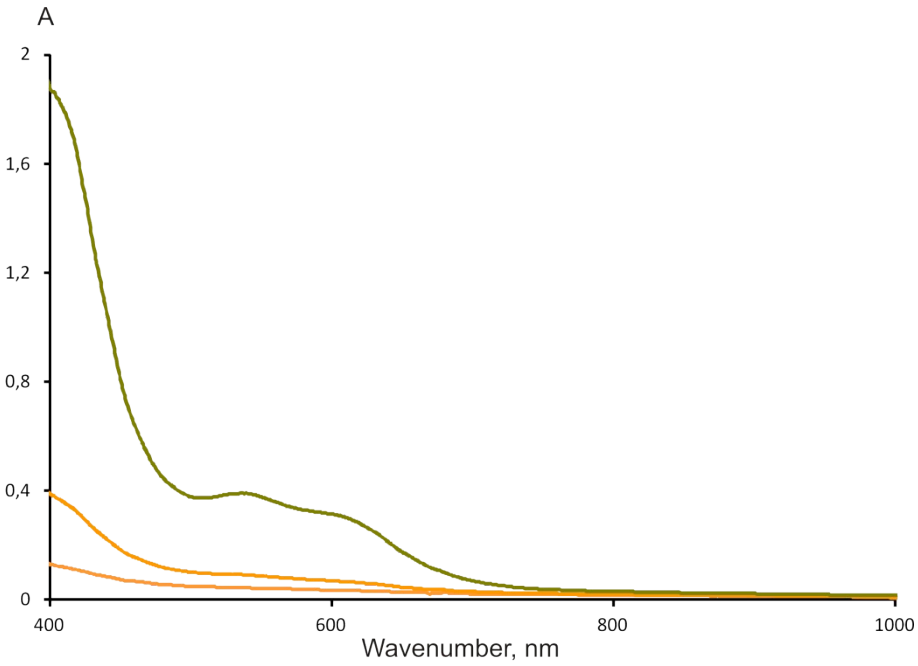

Fig. S4 The UV-Vis spectrum of **3** recorded in THF at room temperature. Green line is for the more concentrated solution.

Luminescence

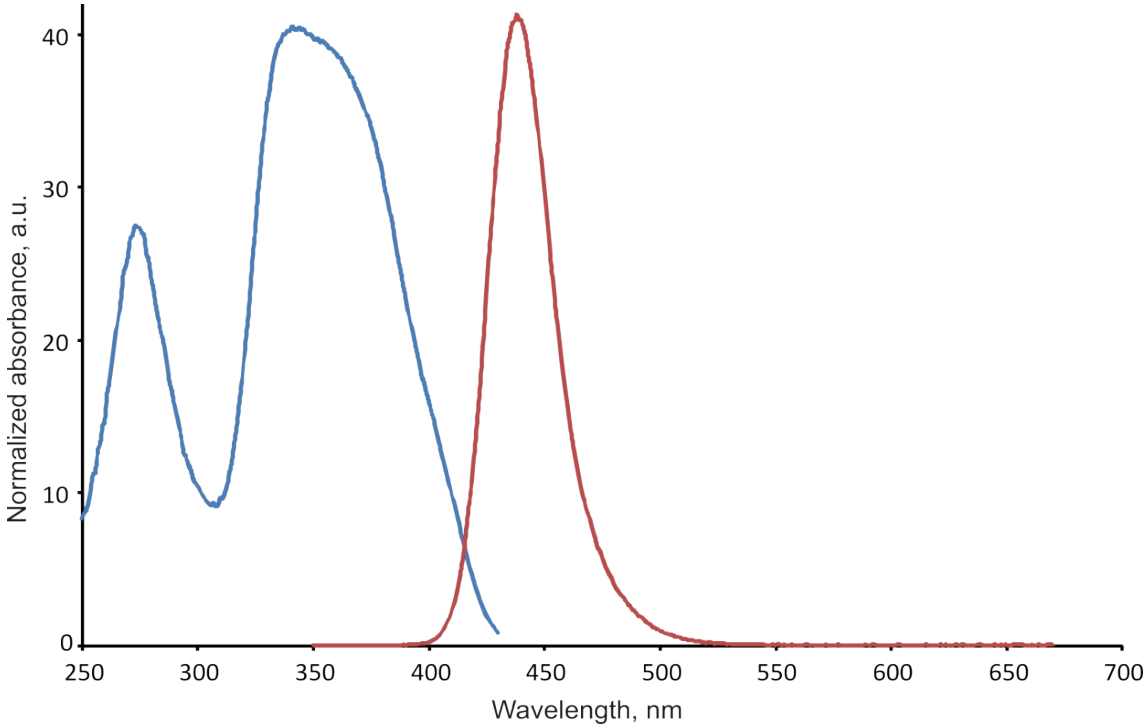

Fig. S5 Room temperature excitation (left, λ_{em} = 440 nm) and emission (right, λ_{ex}= 360 nm) spectra of EuI_2 in THF.

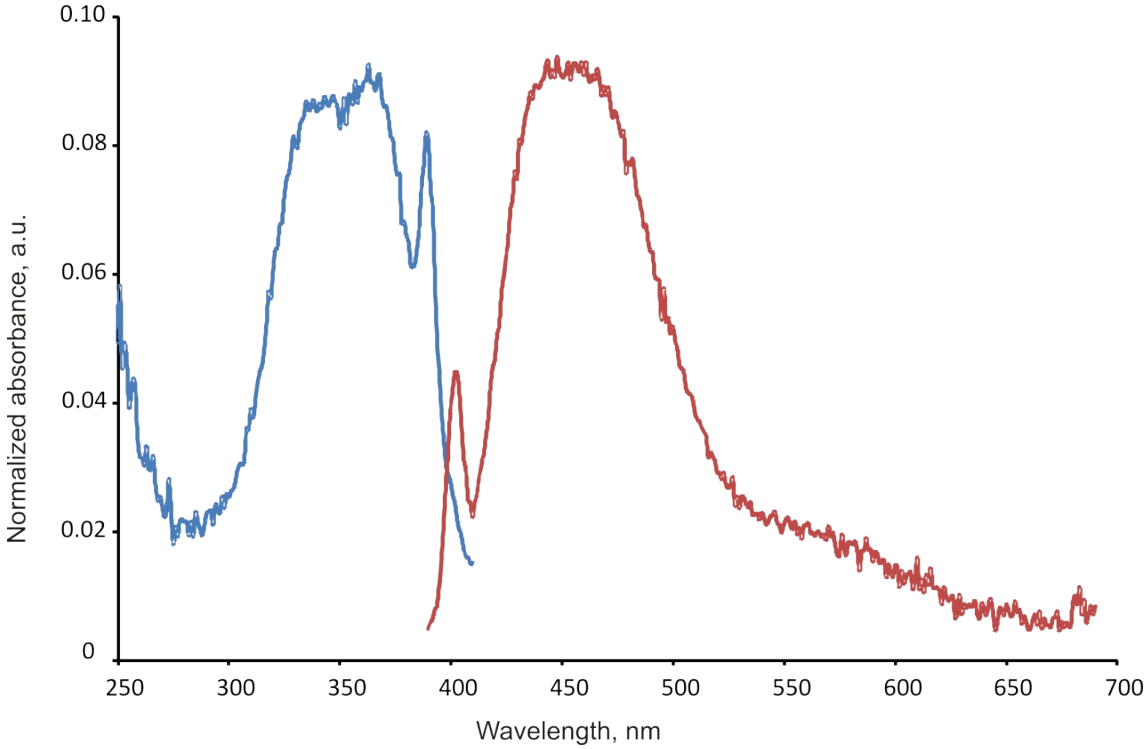

Fig. S6 Room temperature excitation (left, λ_{em} = 440 nm) and emission (right, λ_{ex}= 360 nm) spectra of $[(thf)_2Eu(Ge_9(Hyp)_3)_2]$ in THF.

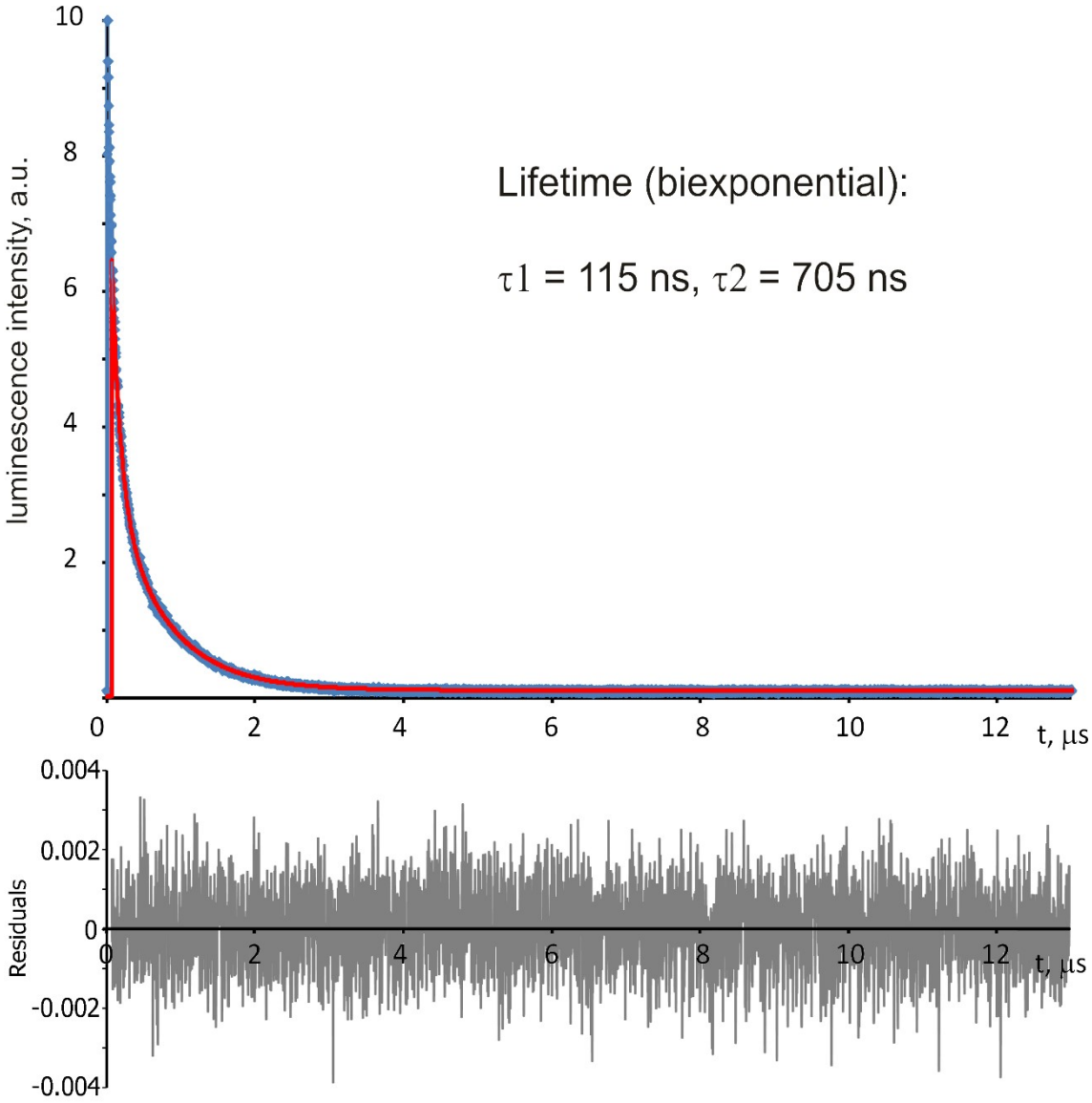

Fig. S7 Luminescence decay (blue scatter) for **2** in THF solution under a dry and deoxygenated argon atmosphere (λ_{ex} = 360 nm, λ_{em} = 440 nm) with monoexponential fit function (red) and instrument response function (grey).

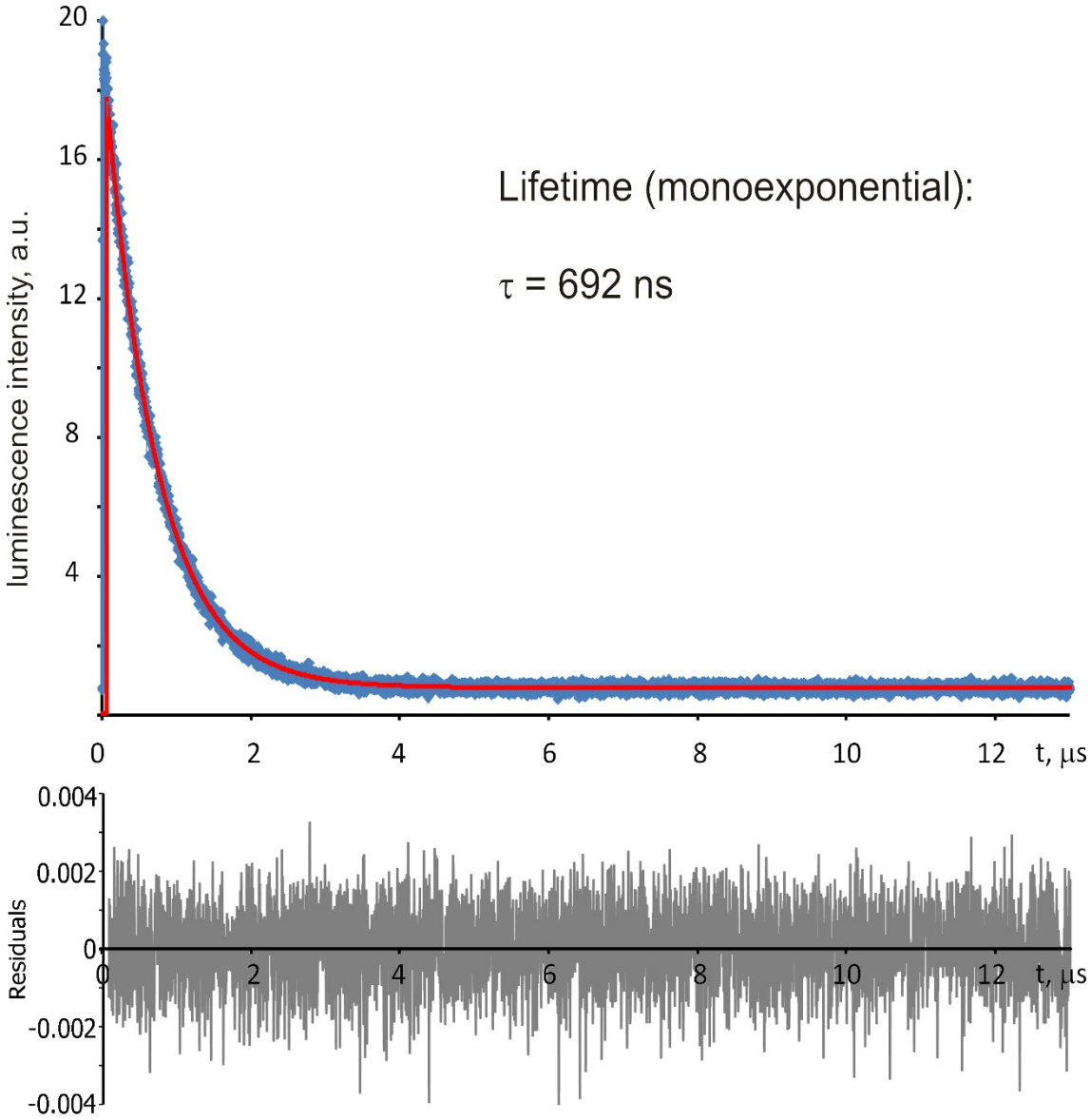

Fig. S8 Luminescence decay (blue scatter) for EuI_2 in THF solution under a dry and deoxygenated argon atmosphere (λ_{ex} = 360 nm, λ_{em} = 440 nm) with monoexponential fit function (red) and instrument response function (grey).

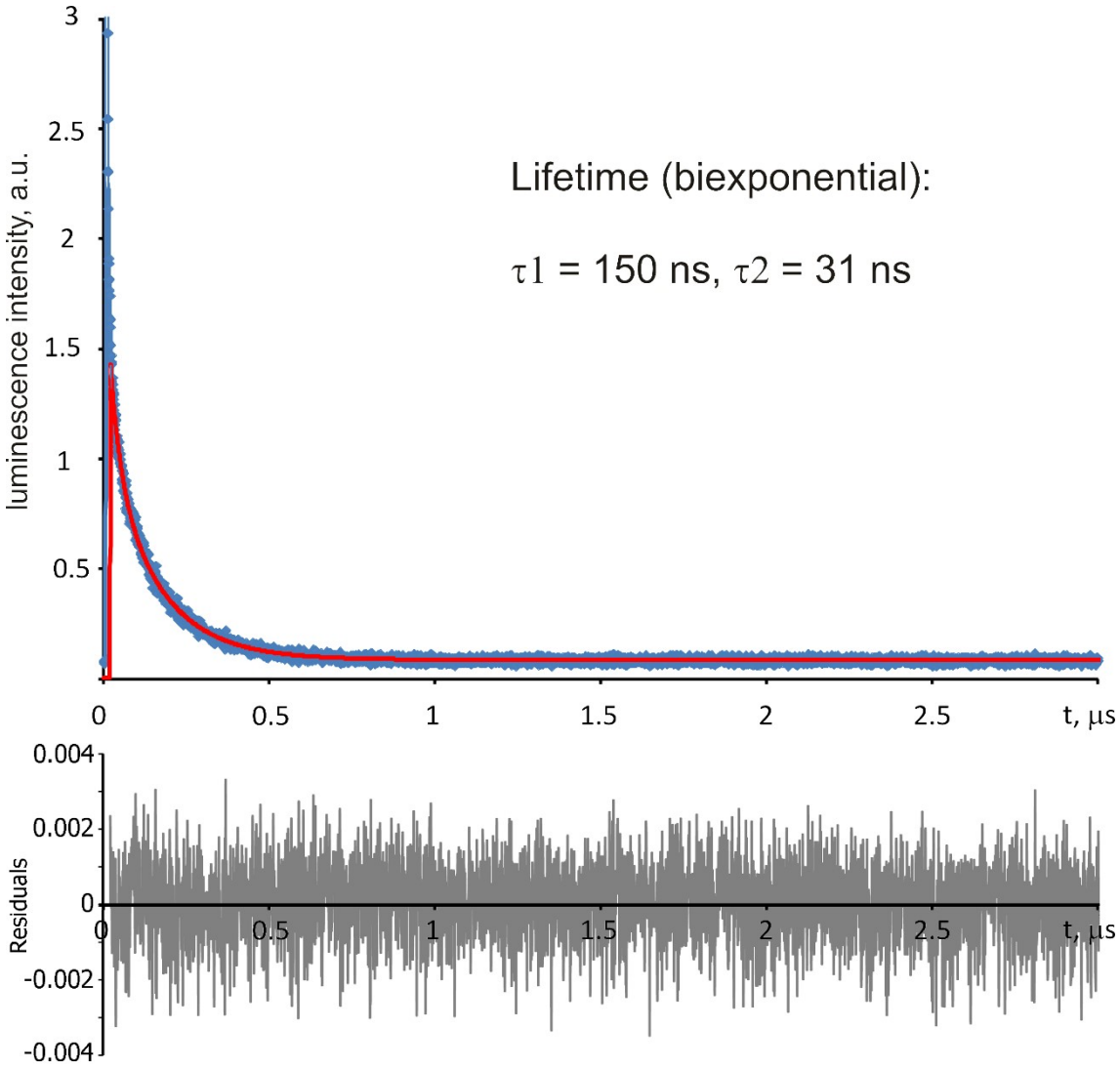

Fig. S9 Luminescence decay (blue scatter) for $[(thf)_2Eu(Ge_9(Hyp)_3)_2]$ in THF solution under a dry and deoxygenated argon atmosphere (λ_{ex} = 360 nm, λ_{em} = 440 nm) with monoexponential fit function (red) and instrument response function (grey).

NMR spectroscopy

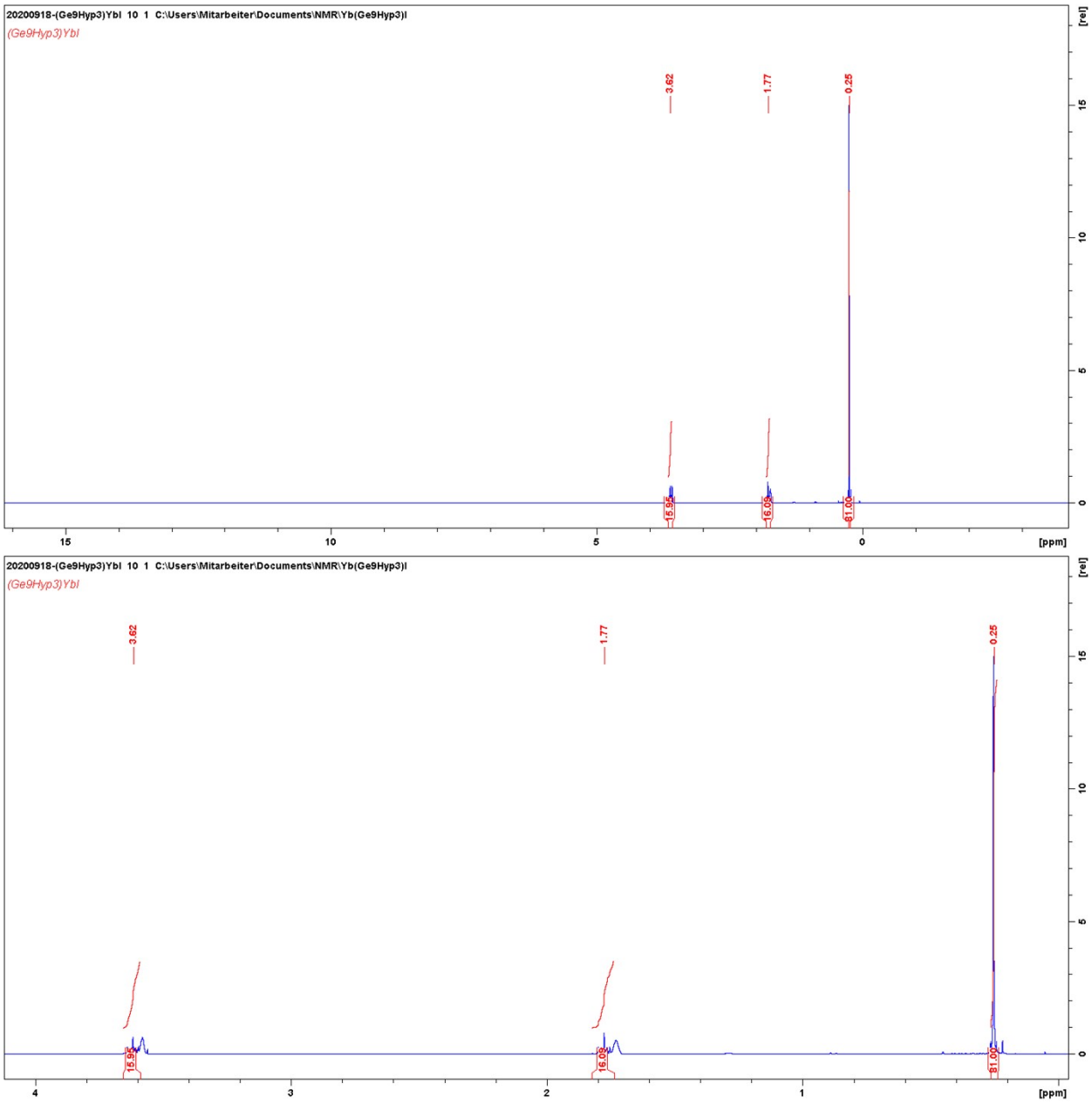

Fig. S10 ^{1}H NMR spectrum of **1** in THF-d_8 (top – full spectrum, bottom – scaled up).

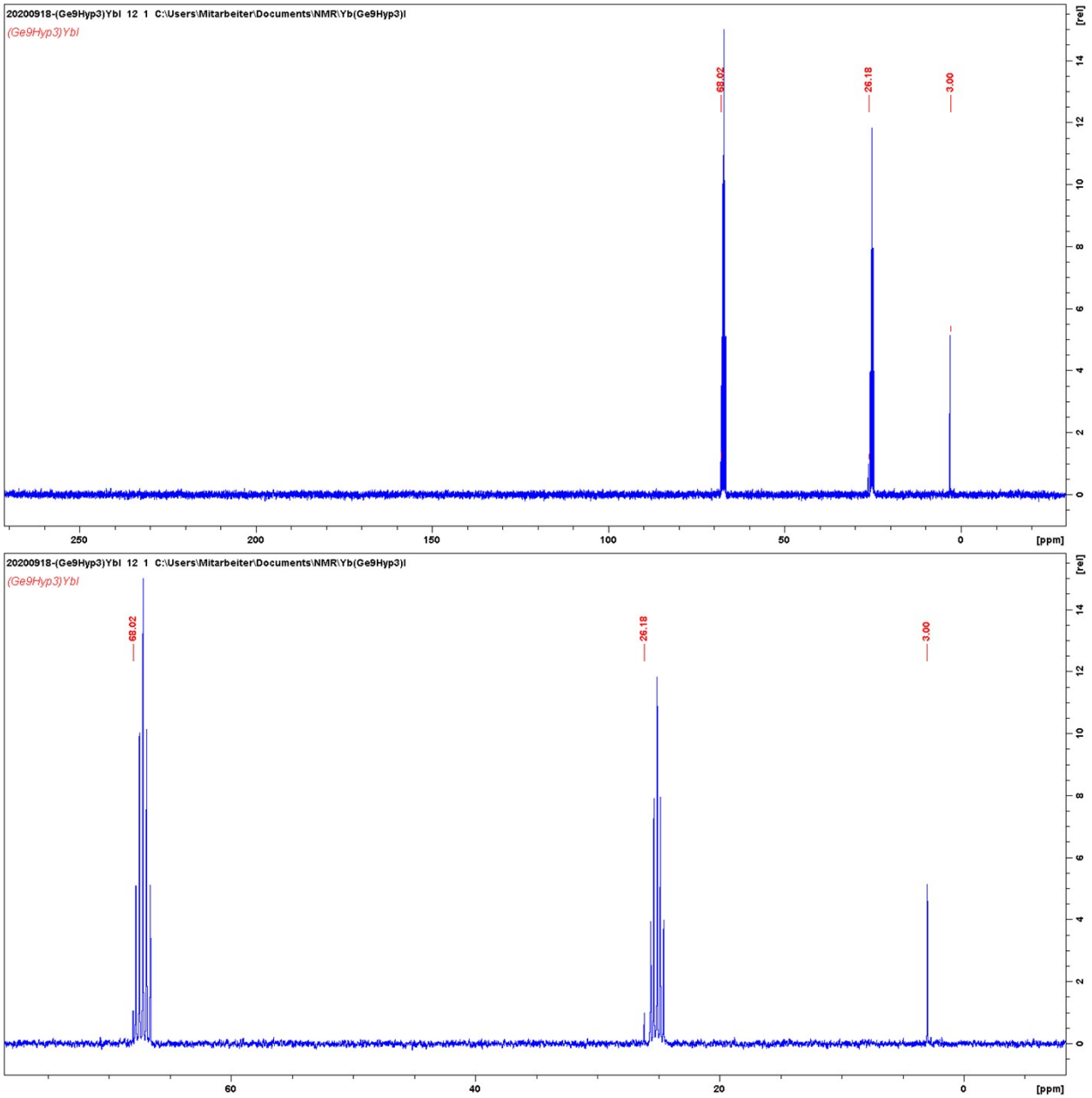

Fig. S11 ^{13}C NMR spectrum of **1** in THF-d_8 (top – full spectrum, bottom – scaled up).

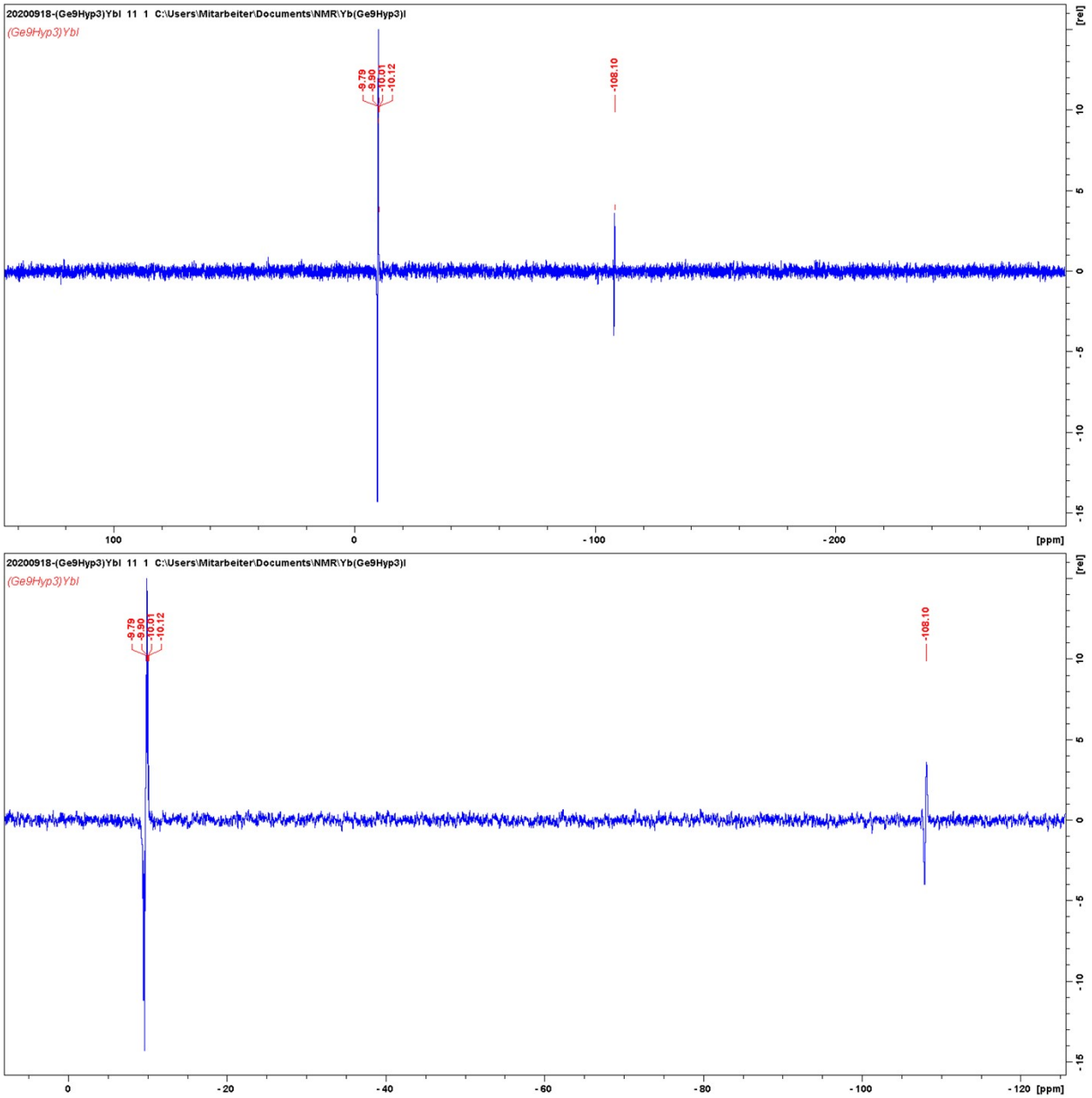

Fig. S12 ^{29}Si NMR spectrum of **1** in THF-d_8 (top – full spectrum, bottom – scaled up).

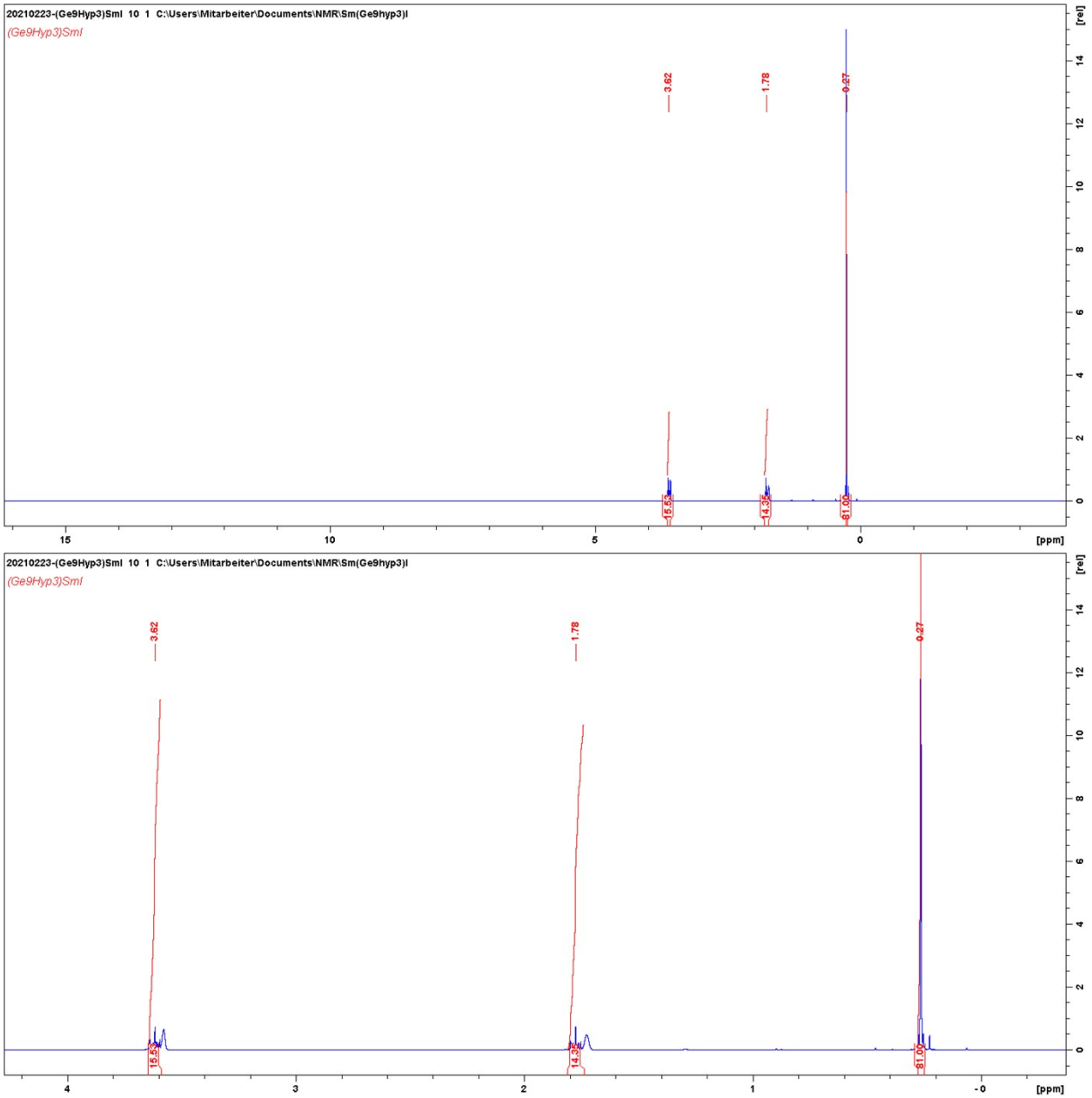

Fig. S13 ^{1}H NMR spectrum of **3** in THF-d_8 (top – full spectrum, bottom – scaled up).

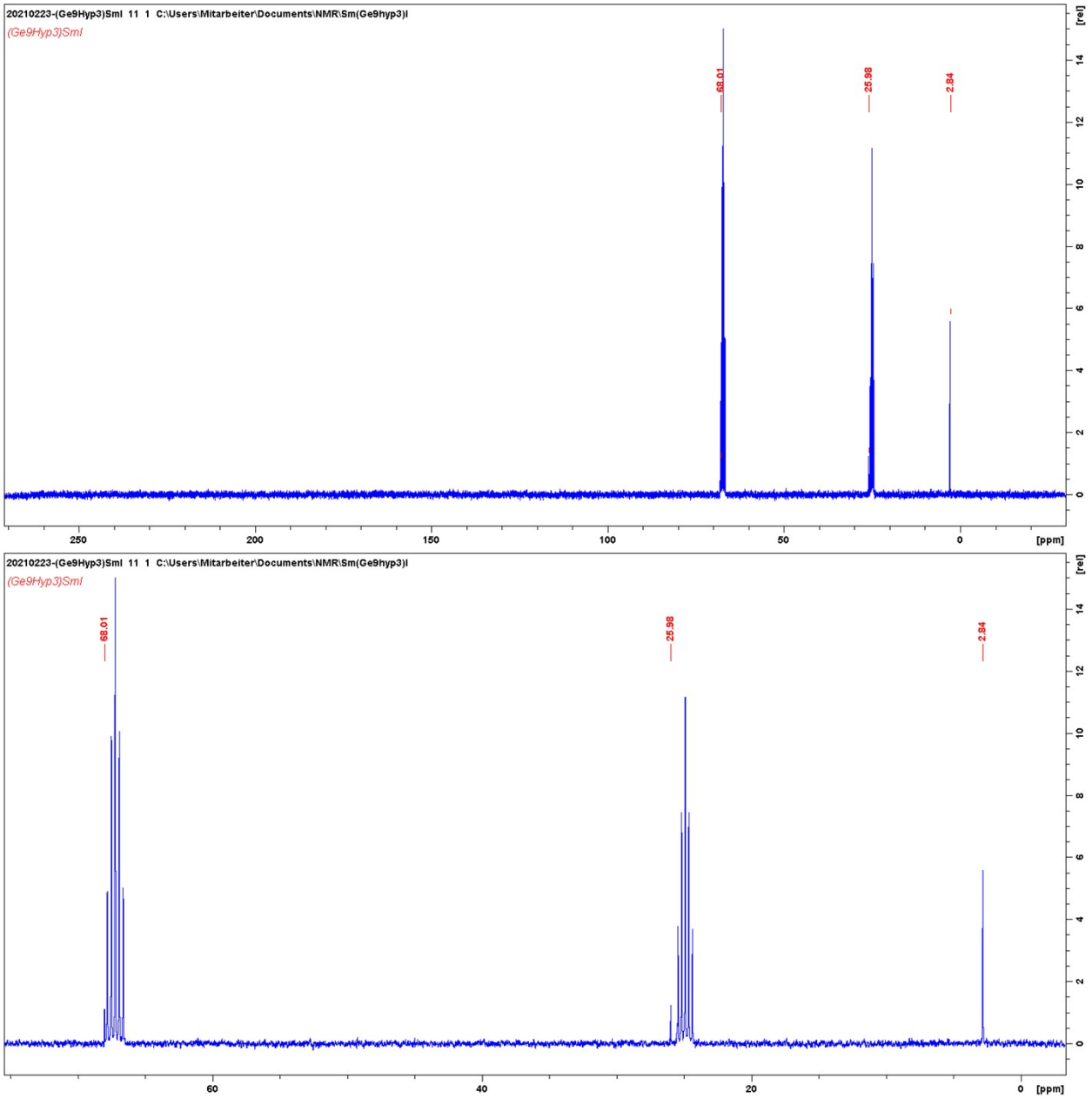

Fig. S14 ^{13}C NMR spectrum of **3** in THF-d_8 (top – full spectrum, bottom – scaled up).

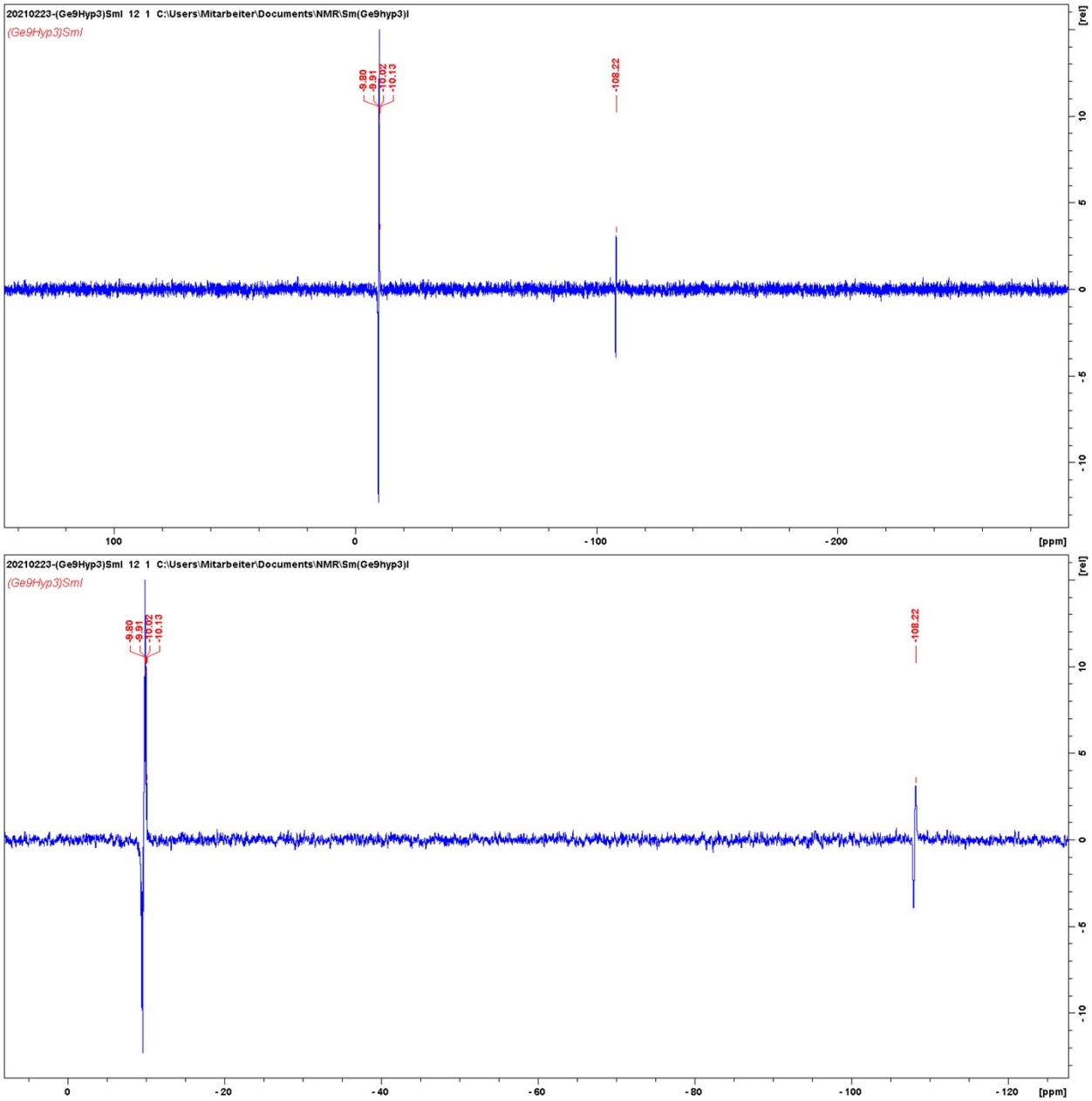

Fig. S15 ^{29}Si NMR spectrum of **3** in THF-d_8 (top – full spectrum, bottom – scaled up).

Additional structure information

The arrangement of the nine germanium atoms as well as bond lengths and angles within anion $[Ge_9(Hyp)_3]^-$ in all compounds **1-3** are almost identical and hardly differ from the geometrical parameters in the lithium[8] and potassium[3] salts with the same anion. The structure of metalloid germanium cluster $[Ge_9(Hyp)_3]^-$ can be described as nearly undistorted tricapped trigonal prism (Fig. S13) with an a:h ratio of 1:1.27 (a – prism base, h – prism height). The bond lengths between the germanium atoms bearing Hyp-ligands (Ge1; Ge2; and Ge3) and the corresponding three naked germanium atoms (Ge4, Ge5, Ge7, Ge8; Ge4, Ge6, Ge7, Ge9; and Ge5, Ge6, Ge8, Ge9, respectively) amount in average to 253 pm. The Ge–Ge distances within the triangular faces of the ligand-free germanium atoms (Ge4-Ge5-Ge6 and Ge7-Ge8-Ge9) vary from 264 to 269 pm, which are somewhat longer.

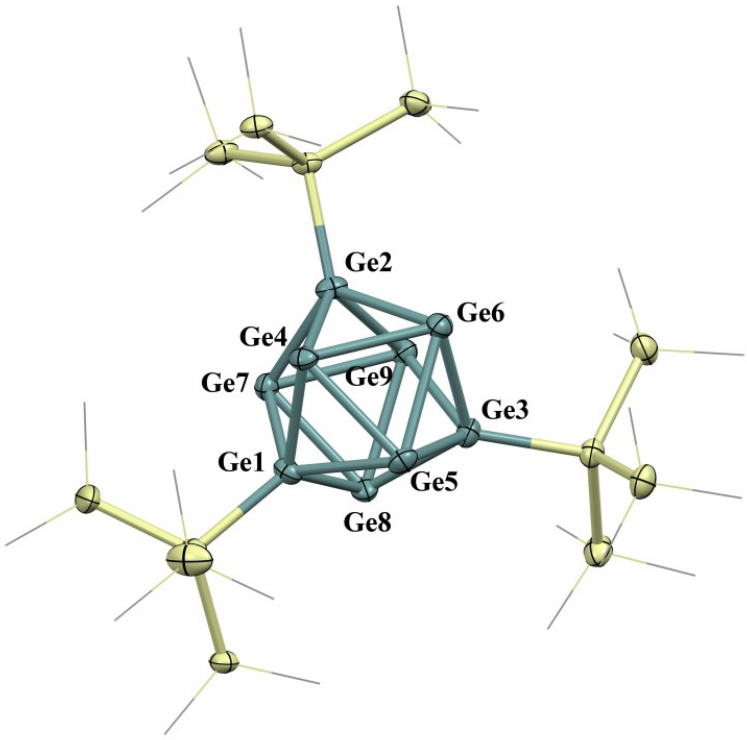

Fig. S16 The structure of anion $[Ge_9(Hyp)_3]^-$ in the compounds **1-3**. Ellipsoids are given in 30% probability.

Table S1: crystallographic details

	1	**2**	**3**
Empirical formula	$C_{86}H_{226}Ge_{18}I_2O_8Si_{24}Yb_2$	$C_{188}H_{484}Eu_4Ge_{36}I_4O_{20}Si_{48}$	$C_{196}H_{500}Ge_{36}I_4O_{22}Si_{48}Sm_4$
Formula weight	3969.31	8142.72	8280.49
T [K]	150.0	200.0	100.0
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [pm]	1415.12(8)	2733.81(3)	2710.8(3)
b [pm]	2416.78(14)	2504.06(3)	2479.6(2)
c [pm]	2583.45(15)	29.0012(3)	2865.5(3)
α [°]	90	90	90
β [°]	93.373(2)	90.3710(10)	90.138(3)
γ [°]	90	90	90
V [Å³]	8820.2(9)	19852.7(4)	19261(3)
Z	2	2	2
ρ_{calc} [g/cm³]	1.495	1.362	1.428
μ [mm^{-1}]	4.611	3.790	3.866
F(000)	3928.0	8120.0	8272.0
Crystal size [mm³]	0.284 × 0.142 × 0.047	0.374 × 0.216 × 0.067	0.249 × 0.108 × 0.056
2θ	3.204 to 52.786	4.082 to 49.5	1.422 to 49.5
Index range	$-17 \le h \le 17$, $-30 \le k \le 30$, $-32 \le l \le 32$	$-32 \le h \le 27$, $-29 \le k \le 29$, $-34 \le l \le 34$	$-31 \le h \le 31$, $-29 \le k \le 29$, $-33 \le l \le 33$
Reflections collected	235660	36629	231890
Independent reflections	18057 [R_{int} = 0.0967, R_{sigma} = 0.0470]	36629 [R_{int} = 0.1342, R_{sigma} = 0.0548]	32967 [R_{int} = 0.1188, R_{sigma} = 0.0834]
Data/restraints/parameters	18057/404/713	36629/501/1308	32967/346/1405
GooF	1.016	1.022	1.029
R [$I \ge 2\sigma(I)$]	0.0421	0.0696	0.0678
R [all data]	0.1123	0.1836	0.1776
Largest peak/hole [e/Å³]	1.15/-1.14	1.30/-0.74	1.59/-1.23
CCDC	**2241576**	**2241575**	**2241577**

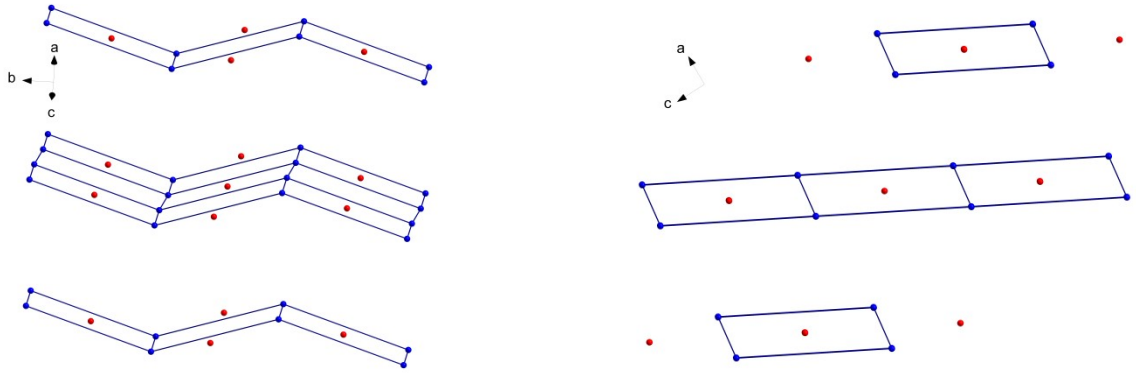

Fig. S17 Left: arrangement of the chessboard sheets in **1**. Right: View along *b* axis illustrating stacking direction in crystallographic a direction. Blue: $[Ge_9(Hyp)_3]^-$, red: $[YbI(thf)_4]_2^{2+}$

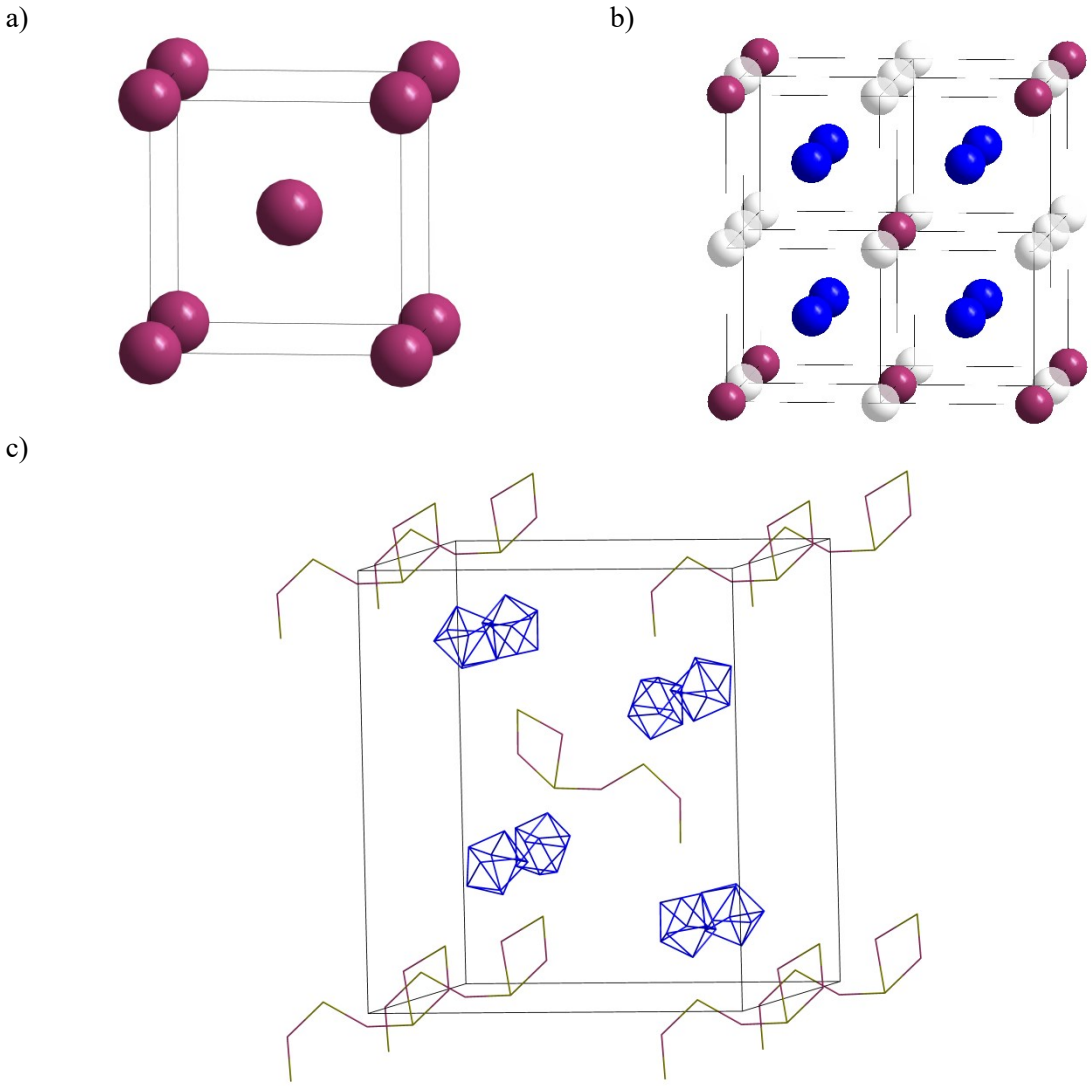

Fig. S18 a) unit cell of W-type, b) 2x2x2 super cell of CsCl. Unoccupied cube edge illustrated as white and transparent, c) unit cell of Sm/Eu with simplified Ge_9 clusters and without coordinating thf molecules

Magnetic measurements

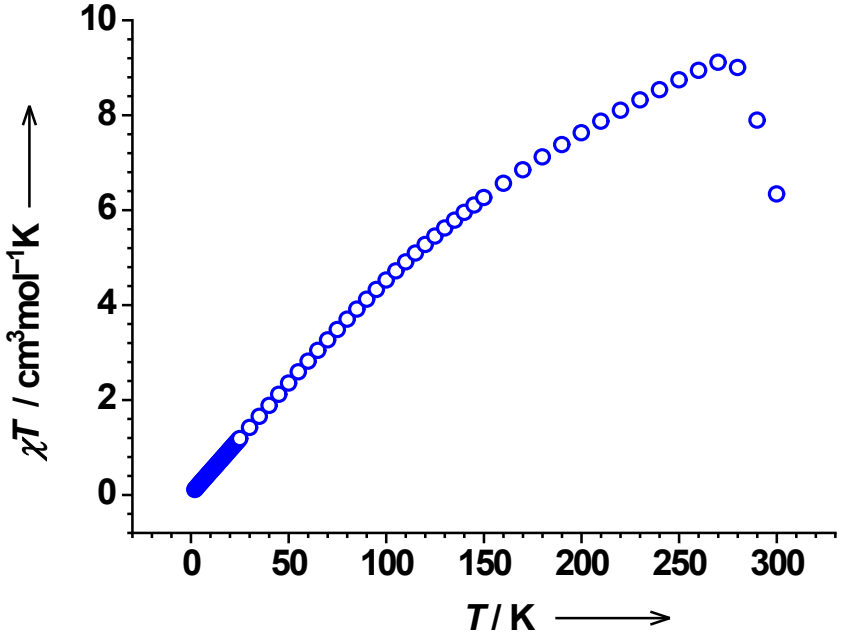

Fig. 19 Variable temperature χT product of **3** measured on a microcrystalline sample at external magnetic field of 0.1 T upon warming.

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