Electronic Supplementary Information

(Part 1)

Combination of single-molecule magnet behaviour and luminescence properties in a new series of lanthanide complexes with tris(pyrazolyl)borate and oligo(β-diketonate) ligands

Elena A. Mikhalyova,[a] Matthias Zeller,[b] Jerry P. Jasinski,[c] Raymond J. Butcher,[d] Luca M. Carrella,[e] Alexander E. Sedykh,[f,g] Konstantin S. Gavrilenko,[h,i] Sergey S. Smola,[j] Michael Frasso,[k] Sebastian C. Cazorla,[b] Kuluni Perera,[b] Anni Shi,[b] Habib G. Ranjbar,[b] Casey Smith,[b] Alexandru Deac,[b] Youlin Liu,[b] Sean M. McGee,[l] Vladimir P. Dotsenko,[j] Michael U. Kumke,[l] Klaus Müller-Buschbaum,[f,g] Eva Rentschler,[e] Anthony W. Addison,*[m] & Vitaly V. Pavlishchuk*[a]

[a] *L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine, Prospekt Nauki 31, Kiev, 03028, Ukraine, tel. (38 044) 525 42 28, fax (38 044) 525 62 16, e-mail: shchuk@inphyschem-nas.kiev.ua;*

[b] *Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN, 47907, U.S.A., e-mail: zeller4@purdue.edu;*

[c] *Department of Chemistry, Keene State College, Keene, NH 03435, USA*

[d] *Chemistry Department Howard University, 525 College St. N.W., Washington, DC 20059, USA*

[e] *Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany*

[f] *Institute of Inorganic and Analytical Chemistry, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany*

[g] *Institute of Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

[h] *Chembiocenter of Taras Shevchenko National University of Kiev, 67 Chervonotkatska St., 02094, Kiev, Ukraine*

[i] *Enamine Ltd, 78 Chervonotkatska St., 02094, Kiev, Ukraine*

[j] *A.V. Bogatsky Physico-Chemical Institute of the National Academy of Sciences of the Ukraine, 86 Lustdorfskaya doroga, 65080 Odessa, Ukraine;*

[k] *Department of Chemistry, 217 Clark Hall West Virginia University, Morgantown, WV, 26508*

[l] *University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany*

[m] *Department of Chemistry, Drexel University, Philadelphia, PA 19104-2816, U.S.A., e-mail: addisona@drexel.edu.*

Experimental

CAUTION: Thallium salts are potentially TOXIC and should be handled with care.

Commercially available reagents and solvents (Aldrich and UkrReaChim) were used without further purification. Thallium hydrotris(pyrazolyl)borate was prepared as described previously.[1] Starting Tp_2LnCl (Ln = Eu, Gd, Tb, Dy) complexes were obtained by reaction of TpTl with the corresponding lanthanide chloride in methanol.[2] H_2Tae, H_2pPhd, H_2mPhd, H_3Pht and HPhm were synthesized according to known procedures.[3-6] C,H,N-microanalyses were performed using a Carlo Erba 1106 analyzer. FAB-LSIMS/CI mass spectra were collected on a Waters Micromass AutoSpec Ultima instrument, using 3-nitrobenzyl alcohol as the matrix; peak assignments are based on the masses of the most abundant isotopes. X-Ray diffraction data were collected on a Rigaku Oxford Diffraction Gemini Eos CCD, a Bruker AXS SMART APEX CCD, or on a Bruker AXS D8 Quest CMOS diffractometer. Structures were solved using SHELXS-97 [7] and refined with the SHELXL (2012 to 2018) [8] by full-matrix least-squares on F^2; H-atoms were treated using a riding model. For details on structure refinement and disorder models, see the ESI. Photo- and electroluminescence spectra were measured using a Perkin-Elmer LS55 luminescence spectrometer, and time-resolved measurements (delay 5 ms) at 77K were collected on a Fluorolog FL 3-22 (HORIBA Jobin-Yvon Inc.) luminescence spectrometer. Photoluminescence quantum efficiencies were determined by the absolute method using a Fluorolog FL 3 (HORIBA Jobin-Yvon Inc.) luminescence spectrometer equipped with a Quanta-φ integrating sphere (HORIBA Jobin-Yvon Inc.). Luminescence decays (at room temperature) were determined by time-correlated single-photon counting (TCSPC) with an FLS920 (Edinburgh Instruments Ltd) fluorescence spectrometer using a microsecond flash lamp as an excitation source and a single-photon avalanche diode (SPAD) as detector. Low temperature (4K) time-resolved luminescence measurements were performed using the boxcar technique. For the excitation, a wavelength tunable pulsed Nd:YAG/OPO laser system (Quanta Ray, Spectra Physics, Mountain View, CA; GWU-Lasertechnik Vertriebsges. mbH, Erftstadt, Germany) operated at a repetition rate of 10 Hz was used. The emission was recorded using an intensified CCD-camera (iStar DH720-18V-73, Andor Technology, Belfast, GB) coupled to a spectrograph (Shamrock SR-303i, Andor Technology, Belfast, U.K.). In order to collect the luminescence decay kinetics, an initial gate delay of $\Delta t = 500$ ns was set between excitation and detection with a gate width of one ms. In a typical time-resolved measurement 10 to 100 laser pulses were accumulated per spectrum, subsequently the initial gate step was increased in steps of one μs (Dy) to 100 μs (Eu). For the low temperature luminescence measurements, a closed cycle liquid helium cryostat (Sumitomo Heavy Industries Ltd, Markt Indersdorf, Germany). Here, the samples were placed in a lab-built copper sample holder in a vacuum chamber (Leybold vacuum Turbolab 80, Oerlikon, Köln, Germany), and a temperature controller (331 temperature controller, Lake Shore, Westerville, OH) was used to set the desired temperature in the range of $4\ K < T < 293\ K$.

Voltage for electroluminescence measurements was applied with a Keithley 2400 Digital Source/Meter and Advanced DC Voltammetry System VERSASTAT4-200.

Magnetic properties (DC and AC) were measured with a Quantum Design MPMS-XL-7 SQUID magnetometer on powdered microcrystalline samples embedded in eicosane to avoid orientation of the crystallites under applied field. The dc magnetic susceptibility values were corrected for diamagnetic susceptibility contribution according to Pascal's constants.[9] The temperature dependent magnetic contribution of the holder and of the embedding matrix eicosane were experimentally determined and substracted from the measured susceptibility data. Variable temperature susceptibility data were collected in a temperature range of 2-300K under an applied field of 0.1 Tesla, while magnetization data were collected between 2 and 10 K and magnetic fields up to 7 Tesla. AC measurements were performed with an oscillating magnetic field of 3 Oe at frequencies ranging from 1 to 1400 Hz at zero *dc* field and with an underlying *dc* magnetic field. The optimum underlying *dc* field for each sample was determined by field-dependent *ac* measurement from zero to 3000 Oe at 2 K. The fields were chosen so that $\Delta\chi'' = (\chi''_{max} - \chi''_{min})$ was maximised, to optimise the signal-to-noise ratio.

Synthesis of Tp_2LnPhm (1Ln, Ln = Eu, Gd, Tb or Dy). 0.5 mmol of Tp_2LnCl and 0.5 mmol of HPhm were dissolved in 10 mL of CH_2Cl_2. Then 0.15 mL of triethylamine was added to this solution and it was stirred for 1 hour. The mixture obtained was filtered and the filtrate was evaporated at low pressure. The resulting residue was washed with water and dried in a vacuum desiccator over P_2O_5. The products obtained were recrystallized from n-heptane or a mixture of $CHCl_3$ and n-hexane. Yield 60-80%. Samples for C,H,N-microanalyses were air-dried, while crystals for X-ray analysis were taken from the subsequent recrystallization's mother liquor immediately before mounting for diffraction. The difference in experimental and calculated C/H/N content for some compounds may result from handling of the sample prior to microanalysis, as *n*-hexane and $CHCl_3$ are very volatile.[10] While some of the properties of **1Eu**, **1Tb** and **1Gd** have been described earlier,[2] the synthesis, crystal structure analyses, detailed emission properties and magnetic data are presented here for the first time.

Tp_2EuPhm (1Eu). Anal. for **1Eu**·$0.75CHCl_3$·$0.25C_6H_{14}$ ($EuC_{31.25}H_{35.25}N_{12}B_2O_2Cl_{2.25}$) calcd/found: C 43.4/43.5, H 4.08/3.92, N 19.4/19.4. Mass spectrum, FAB^+ (m/z): 753.2 (0.2%, $[1Eu\text{-}H^-]^+$, calcd 753.2); 687.1 (18%, $[(Tp\text{-}pz)TpEuPhm]^+$, calcd 687.2); 579.1 (100%, $[Tp_2Eu]^+$, calcd 579.1); 541.0 (45%, $[TpEuPhm]^+$, calcd 541.1). X-ray quality crystals of composition **1Eu**·C_6H_{14} were obtained by recrystallization from n-hexane.

Tp_2GdPhm (1Gd). Anal. for **1Gd**·$0.65CHCl_3$·$0.65C_6H_{14}$ ($GdC_{33.55}H_{40.75}N_{12}B_2O_2Cl_{1.95}$) calcd/found: C 45.2/45.2, H 4.57/4.13, N 18.8/18.6. Mass spectrum, FAB^+ (m/z): 758.1 (0.1%, $[1Gd\text{-}H^-]^+$, calcd 758.2); 690.1 (16%, $[(Tp\text{-}pz)TpGdPhm]^+$, calcd 691.2); 583.1 (100%, $[Tp_2Gd]^+$, calcd 582.1); 546.0 (45%, $[TpGdPhm]^+$, calcd 546.1). X-ray quality crystals of composition **1Gd**·C_7H_{16} were obtained by recrystallization from n-heptane.

Tp_2TbPhm (1Tb). Anal. for **1Tb**·0.6$CHCl_3$·0.6C_6H_{14} ($TbC_{33.2}H_{40}N_{12}B_2O_2Cl_{1.8}$) calcd/found: C 45.1/45.3, H 4.53/4.16, N 19.0/18.8. Mass spectrum, FAB^+ (m/z): 759.1 (0.1%, $[1Tb\text{-}H^-]^+$, calcd 759.2); 693.1 (11%, $[(Tp\text{-}pz)TpTbPhm]^+$, calcd 693.2); 585.0 (100%, $[Tp_2Tb]^+$, calcd 585.1); 547.0 (46%, $[TpTbPhm]^+$, calcd 547.1). X-ray quality crystals of composition **1Tb** were obtained by recrystallization from n-heptane.

Tp_2DyPhm (1Dy). Anal. for **1Dy**·1.6$CHCl_3$·0.4C_6H_{14} ($DyC_{33}H_{38.2}N_{12}B_2O_2Cl_{4.8}$) calcd/found: C 40.0/39.9, H 3.86/4.08, N 17.0/17.0. Mass spectrum, CI (m/z): 763.2 (5%, $[1Dy\text{-}H^-]^+$, calcd 763.2); 697.3 (100%, $[(Tp\text{-}pz)TpDyPhm]^+$, calcd 697.2); 589.3 (90%, $[Tp_2Dy]^+$, calcd 589.1). X-ray quality crystals of composition **1Dy** were obtained by recrystallization from n-heptane.

Synthesis of $(Tp_2Ln)_2L$ (Ln = Eu, Gd, Tb or Dy, 2Ln, L^{2-} = Tae^{2-}; 3Ln, L^{2-} = $pPhd^{2-}$; 4Ln, L^{2-} = $mPhd^{2-}$). These complexes were obtained in the same manner as **1Ln**, but using 0.25 mmol of the corresponding H_2L instead of Phm. Yield 60-80%. Crystals for X-ray analysis were taken from the mother liquor immediately before mounting for diffraction, while samples for C,H,N-microanalyses were air-dried.

$(Tp_2Eu)_2$Tae (2Eu). Anal. for **2Eu**·0.5 C_6H_{14} ($C_{49}H_{59}N_{24}O_4B_4Eu_2$) calcd/found: C 42.2/42.4, H 4.23/4.37, N 24.1/23.8. Mass spectrum, FAB^+ (m/z): 1352.1 (1%, $[2Eu]^+$, calcd 1352.3); 1285.1 (1%, $[2Eu\text{-}pz]^+$, calcd 1285.3); 579.1 (100%, $[Tp_2Eu]^+$, calcd 579.1).). X-ray quality crystals of composition **2Eu**·1.875 C_7H_8·1.5 C_6H_{14} were obtained by slow diffusion of n-hexane into a toluene solution of the compound.

$(Tp_2Gd)_2$Tae (2Gd). Anal. for **2Gd**·0.75 $CHCl_3$·0.5 C_6H_{14} ($C_{49.75}H_{59.75}N_{24}O_4B_4Gd_2Cl_{2.25}$) calcd/found: C 39.9/39.8, H 4.00/3.88, N 22.5/22.5. X-ray quality crystals of composition **2Gd**·3.5 C_7H_8 were obtained by slow diffusion of n-heptane into a toluene solution of the compound.

$(Tp_2Tb)_2$Tae (2Tb). Anal. for **2Tb**·$CHCl_3$·0,5 C_6H_{14} ($C_{53}H_{67}N_{24}O_4B_4Tb_2Cl_3$) calcd/found: C 40.5/40.7, H 4.26/3.85, N 21.4/21.4. Mass spectrum, FAB^+ (m/z): 1366.4 (2%, $[2Tb]^+$, calcd 136.4), 1299.4 (1%, $[2Tb\text{-}pz]^+$, calcd 1299.3), 585.1 (100%, $[Tp_2Tb]^+$, calcd 585.1). X-ray quality crystals of composition **2Tb**·0.924 C_6H_{14}·2.592 C_6H_{12} were obtained by slow diffusion of mixed hexanes into CH_2Cl_2 solution of the compound.

$(Tp_2Dy)_2$Tae (2Dy). Anal. for **2Dy**·1.5 $CHCl_3$·0.5 C_6H_{14} ($C_{50.5}H_{60.5}N_{24}O_4B_4Dy_2Cl_{4.5}$) calcd/found: C 38.0/37.9, H 3.79/4.17, N 21.1/20.9. Mass spectrum, CI (m/z): 1373.5 (<1%, $[2Dy]^+$, calcd 1373.3), 1306.1 (<1%, $[2Dy\text{-}pz]^+$, calcd 1306.3), 589.3 (100%, $[Tp_2Dy]^+$, calcd 589.1). X-ray quality crystals of composition **2Dy**·C_7H_8 were obtained by slow diffusion of n-hexane into a toluene solution of the compound.

$(Tp_2Eu)_2$pPhd (3Eu). Anal. for **3Eu**·0.4 $CHCl_3$ ($C_{52.4}H_{56.4}N_{24}O_4B_4Eu_2Cl_{1.2}$) calcd/found: C 42.6/41.4, H 3.82/3.77, N 22.8/22.9. Mass spectrum, FAB^+ (m/z): 1429.2 (1%, $[3Eu+H^+]^+$, calcd 1429.4), 1361.2 (6%, $[3Eu\text{-}pz]^+$, calcd 1361.3), 1215.1 (2%, $[Tp_2EupPhdEuTp]^+$, calcd 1215.3), 1070.1 (1%, $[Tp_2EupPhdEupz]^+$, calcd 1069.2), 579.1 (100%, $[Tp_2Eu]^+$, calcd 579.1). X-ray quality crystals

of composition **3Eu**·2 CH_2Cl_2 were obtained by slow diffusion of n-hexane into a CH_2Cl_2 solution of the compound.

$(Tp_2Gd)_2pPhd$ (3Gd). Anal. for **3Gd**·1.5 $CHCl_3$ ($C_{53.5}H_{57.5}N_{24}O_4B_4Gd_2Cl_{4.5}$) calcd/found: C 39.7/38.7, H 3.56/3.63, N 20.8/20.8. X-ray quality crystals of composition **3Gd**·3 C_7H_8 were obtained by slow diffusion of n-hexane into a toluene solution of the compound.

$(Tp_2Tb)_2pPhd$ (3Tb). Anal. for **3Tb**·1.5 $CHCl_3$·0.5 C_6H_{14} ($C_{56.5}H_{64.5}N_{24}O_4B_4Tb_2Cl_{4.5}$) calcd/found: C 40.7/40.6, H 3.88/3.60, N 20.2/19.8. Mass spectrum, FAB^+ (m/z): 1442.8 (<0.5%, $[3Tb]^+$, calcd 1442.4), 1375.6 (1%, $[3Tb\text{-}pz]^+$, calcd 1375.4), 1229.5 (1%, $[Tp_2TbpPhdTbTp]^+$, calcd 1229.3), 1083.5 (1%, $[Tp_2TbpPhdTbpz]^+$, calcd 1083.2), 585.4 (100%, $[Tp_2Tb]^+$, calcd 585.1). X-ray quality crystals of composition **3Tb**·3 C_7H_8 were obtained by slow diffusion of n-hexane into a toluene solution of compound.

$(Tp_2Dy)_2pPhd$ (3Dy). Anal. for **3Dy**·1.75 $CHCl_3$ ($C_{53.75}H_{57.75}N_{24}O_4B_4Dy_2Cl_{5.25}$) calcd/found: C 38.9/37.0, H 3.48/4.08, N 20.3/20.2. Mass spectrum, CI (m/z): 1448.2 (1%, $[3Dy\text{-}H^-]^+$, calcd 1448.2), 1382.3 (20%, $[3Dy\text{-}pz]^+$, calcd 1382.3), 1236.3 (10%, $[Tp_2DypPhdDyTp]^+$, calcd 1236.4), 589.4 (100%, $[Tp_2Dy]^+$,calcd 589.1). X-ray quality crystals of composition **3Dy**·3 C_7H_8 were obtained by slow diffusion of n-hexane into a toluene solution of compound.

$(Tp_2Eu)_2mPhd$ (4Eu). Anal. for **4Eu** ($C_{52}H_{56}N_{24}O_4B_4Eu_2$) calcd/found: C 43.7/43.3, H 3.92/4.00, N 23.5/24.2. We are unable to rationalise the difference (0.7%) between experimental and calculated N content, which is greater than we'd like to see, but since this compound was obtained in the same manner as other similar complexes and MS and X-Ray analysis confirmed its structure, we are reasonably confident that this is the target compound. Mass spectrum, FAB^+ (m/z): 1360.3 (0.5%, $[4Eu\text{-}pz]^+$, calcd 1361.3), 1215.2 (1%, $[Tp_2EumPhdEuTp]^+$, calcd 1215.3), 1069.2 (0.3%, $[Tp_2EumPhdEupz]^+$, calcd 1069.2), 577.1 (100%, $[Tp_2Eu]^+$, calcd 579.1). X-ray quality crystals of composition **4Eu**·1.5 C_7H_8 were obtained by slow diffusion of n-hexane into a toluene solution of the compound.

$(Tp_2Gd)_2mPhd$ (4Gd). Anal. for **4Gd**·$CHCl_3$·0.75 C_6H_{14} ($C_{57.5}H_{67.5}N_{24}O_4B_4Gd_2Cl_3$) calcd/found: C 42.5/42.7, H 4.16/4.21, N 20.7/21.0. X-ray quality crystals of composition **4Gd**·C_7H_{14} were obtained by recrystallization from mixed heptanes.

$(Tp_2Tb)_2mPhd$ (4Tb). Anal. for **4Tb**·$CHCl_3$·C_6H_{14} ($C_{59}H_{71}N_{24}O_4B_4Tb_2Cl_3$) calcd/found: C 43.0/43.0, H 4.31/3.82, N 20.4/20.0. Mass spectrum, FAB^+ (m/z): 1442.2 (<0.5%, $[4Tb]^+$, calcd 1442.4), 1375.2 (1%, $[4Tb\text{-}pz]^+$, calcd 1375.4), 1229.1 (2%, $[Tp_2TbmPhdTbTp]^+$, calcd 1229.3), 1083.1 (1.2%, $[Tp_2TbmPhdTbpz]^+$, calcd 1083.2), 585.0 (100%, $[Tp_2Tb]^+$, calcd 585.1). X-ray quality crystals of composition **4Tb**·1.5 C_7H_8 were obtained by slow diffusion of n-hexane into a toluene solution of the compound.

$(Tp_2Dy)_2mPhd$ (4Dy). Anal. for **4Dy**·3 CH_2Cl_2 ($C_{55}H_{62}N_{24}O_4B_4Dy_2Cl_6$) calcd/found: C 38.7/38.9, H 3.64/4.65, N 19.7/19.9. Mass spectrum, CI (m/z): 1449.3 (1%, $[4Dy]^+$, calcd 1449.2), 1382.3 (20%, $[4Dy\text{-}pz]^+$, calcd 1382.3), 589.4 (100%, $[Tp_2Dy]^+$, calcd 589.1). X-ray quality crystals

of composition **4Dy**·1.5 C_7H_8 were obtained by slow diffusion of n-hexane into a toluene solution of the compound.

Synthesis of $(Tp_2Ln)_3Pht$ (5Ln, Ln = Eu, Gd, Tb or Dy). These complexes were obtained in the same manner as **Tp_2LnPhm**, but using 0.17 mmol of H_3Pht instead of Phm. Yield 60-80%. Crystals for X-ray analysis were taken from the recrystallization mother liquor immediately before mounting for diffraction, while samples for C,H,N-microanalyses were air-dried.

$(Tp_2Eu)_3Pht$ (5Eu). Anal. for **5Eu**·1.25 $CHCl_3$·3 C_6H_{14} ($C_{94.25}H_{124.25}N_{36}O_6B_6Eu_3Cl_{3.75}$) calcd/found: C 45.1/45.3, H 4.95/4.56, N 20.1/19.9. Mass spectrum, FAB^+ (m/z): 2103.6 (<0.5%, $[5Eu]^+$, calcd 2103.5), 2035.8 (<0.5%, $[5Eu\text{-}pz]^+$, calcd 2036.5), 1891.5 (<0.5%, $[(Tp_2Eu)_2PhtEuTp]^+$, calcd 1890.4), 1459.3 (<0.5%, $[Tp_2EuPhdEuTp_2\text{-}pz+H]^+$, calcd 1459.4), 1313.3 (<0.5%, $[Tp_2EuPhtEuTp+H]^+$, calcd 1313.3), 579.1 (100%, $[Tp_2Eu]^+$, calcd 579.1). X-ray quality crystals of composition **5Eu**·C_7H_8 were obtained by diffusion of n-heptane into a toluene solution of the compound.

$(Tp_2Gd)_3Pht$ (5Gd). Anal. for **5Gd**·1.5 $CHCl_3$ ($C_{76.5}H_{82.5}N_{36}O_6B_6Gd_3Cl_{4.5}$) calcd/found: C 40.0/39.9, H 3.59/3.67, N 21.9/21.6. X-ray quality crystals of composition **5Gd**·C_7H_8 were obtained by diffusion of n-heptane into a toluene solution of the compound.

$(Tp_2Tb)_3Pht$ (5Tb). Anal. for **5Tb**·2 $CHCl_3$·16 H_2O ($C_{77}H_{115}N_{36}O_{22}B_6Tb_3Cl_6$) calcd/found: C 34.9/34.8, H 4.34/4.15, N 19.0/19.1. Mass spectrum, FAB^+ (m/z): 2122.7 (<0.5%, $[5Tb]^+$, calcd 2124.6), 2056.8 (1%, $[5Tb\text{-}pz]^+$, calcd 2057.5), 1911.5 (0.5%, $[(Tp_2Tb)_2PhtTbTp]^+$, calcd 1911.4), 1473.3 (0.5%, $[Tp_2TbPhtTbTp_2\text{-}pz+H]^+$, calcd 1473.4), 1045.1 (1%, $[TpTbPhtTbTp\text{-}pz\text{-}H]^+$, calcd 1045.2), 585.1 (100%, $[Tp_2Tb]^+$, calcd 585.1). X-ray quality crystals of composition **5Tb**·0.134 CH_2Cl_2·0.224 H_2O were obtained by diffusion of n-hexane into a CH_2Cl_2 solution of the compound.

$(Tp_2Dy)_3Pht$ (5Dy). Anal. for **5Dy**·3 $CHCl_3$·5 H_2O ($C_{78}H_{94}N_{36}O_{11}B_6Dy_3Cl_9$) calcd/found: C 36.2/36.0, H 3.64/3.81, N 19.5/19.6. Mass spectrum, CI (m/z): 1921.3 (<5%, $[(Tp_2Dy)_2PhtDyTp]^+$, calcd 1922.0), 589.4 (100%, $[Tp_2Dy]^+$, calcd 589.1). X-ray quality crystals of composition **5Dy**·4C_7H_8·0.5C_7H_{16} were obtained by diffusion of n-heptane into a toluene solution of the compound.

Procedure for LED cell construction. The substrate, an ITO-coated glass with a sheet resistance of 16 Ω/cm^2, was washed with distilled water and isopropyl alcohol in an ultrasonic bath. PVK (poly(N-vinylcarbazole)) and the target complex were dissolved in chloroform to produce solutions of 15 mg/mL and 4-6 mg/mL, respectively. The chloroform solutions of PVK and the target complex were spin-coated sequentially, twice (1500 rpm, 30 s) onto the ITO substrate to prepare a light-emitting layer. Aluminium, as a cathode layer, was subsequently deposited onto the emission layer by the conventional vacuum deposition procedure.

Table S1. Crystal data and structure refinement for **Tp_2LnPhm** (**1Ln**) and **$(Tp_2Ln)_2Tae$** (**2Ln**)

Compound	**1Eu·C_6H_{14}·solvent**	**1Gd·C_7H_{16}**	**1Tb·solvent**	**1Dy·C_7H_{16}**	**2Eu·1.849 C_7H_8·1.5 C_6H_{14}**	**2Gd·3.5 C_7H_8**	**2Tb·0.924 C_6H_{14}·2.592 C_6H_{12}**	**2Dy·C_7H_8**
Empirical formula	$C_{35}H_{45}B_2EuN_{12}O_2$	$C_{36}H_{47}B_2GdN_{12}O_2$	$C_{29}H_{31}B_2N_{12}O_2Tb$	$C_{36}H_{47}B_2DyN_{12}O_2$	$C_{67.94}H_{87.79}B_4Eu_2N_{24}O_4$	$C_{141}H_{160}B_8Gd_4N_{48}O_8$	$C_{67.10}H_{96.05}B_4N_{24}O_4Tb_2$	$C_{53}H_{60}B_4Dy_2N_{24}O_4$
Moiety formula	$C_{29}H_{31}B_2EuN_{12}O_2$, C_6H_{14}	$C_{29}H_{31}B_2GdN_{12}O_2$, C_7H_{16}	$C_{29}H_{31}B_2N_{12}O_2Tb$	$C_{29}H_{31}B_2DyN_{12}O_2$, C_7H_{16}	$C_{46}H_{52}B_4Eu_2N_{24}O_4$, 1.849($C_7H_8$), 1.5($C_6H_{10}$)	2(C_{46} $H_{52}B_4Gd_2N_{24}O_4$), 7(C_7H_8)	$C_{46}H_{52}B_4N_{24}O_4Tb_2$, 0.924($C_6H_{14}$), 2.592($C_6H_{12}$)	$C_{46}H_{52}B_4Dy_2N_{24}O_4$, C_7H_8
Formula weight	839.41	858.72	760.20	863.97	1651.85	3370.64	1663.98	1465.49
Temperature	100(2)	150(2)	100(2)	173(2)	150(2)	150(2)	100(2)	100(2)
Wavelength	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	C2/c	C2/c	C2/c	I 2/a	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 15.9362(5)Å b = 22.9093(7)Å c = 11.4830(4)Å α = 90° β = 112.1960(10)° γ = 90°	a = 15.7647(8)Å b = 23.1997(10)Å c = 11.4127(6)Å α = 90° β = 111.495(2)° γ = 90°	a = 15.7398(9) Å b = 23.0751(10) Å c = 11.3694(15) Å α = 90° β = 111.416(3)° γ = 90°	a = 11.3834(5) Å b = 23.2108(10) Å c = 15.7395(7) Å α = 90° β = 111.121(5)° γ = 90°	a = 15.3596(10) Å b = 15.8399(10) Å c = 19.0548(8) Å α = 68.0930(13)° β = 69.8068(18)° γ = 69.0277(13)°	a = 15.3014(8)Å b = 16.0243(8)Å c = 19.0473(9)Å α = 66.9030(10)° β = 69.9110(10)° γ = 69.3380(10)°	a = 15.4693(12)Å b = 15.8266(12)Å c = 18.8399(14)Å α = 68.3610(10)° β = 69.3610(10)° γ = 69.3760(10)°	a = 13.3869(4)Å b = 15.1537(5)Å c = 17.5408(6)Å α = 108.8448(13)° β = 107.2054(12))° γ = 93.7594(14)°
Volume, $Å^3$	3881.6(2)	3883.7(3)	3844.2(6)	3879.3(3)	3894.5(4)	3903.9(3)	3879.1(5)	3165.41(18)
Z	4	4	4	4	2	1	2	2
Density (calcd.), g/cm^3	1.436	1.469	1.313	1.308	1.409	1.434	1.425	1.538
Absorption coefficient, mm^{-1}	1.664	1.757	1.880	10.630	1.657	1.746	1.869	12.999
F(000)	1712	1748	1520	1524	1683	1702	1697.2	1460
Crystal size, mm	0.35 × 0.21 × 0.09	0.34 × 0.26 × 0.20	0.25 × 0.21 × 0.12	0.41 × 0.37 × 0.21	0.22 × 0.21 × 0.14	0.36 × 0.19 × 0.11	0.52 × 0.32 × 0.13	0.21 × 0.13 × 0.11
Theta range for data collection	2.614 to 28.281	3.252 to 33.214	2.611 to 26.372	3.562 to 71.623	2.3783 to 33.2608	3.270 to 30.592	1.45 to 31.93	2.826 to 80.175
Index ranges	-19 ≤ h ≤ 21 -30 ≤ k ≤ 30 -15 ≤ l ≤ 15	-24 ≤ h ≤ 24 -35 ≤ k ≤ 35 -17 ≤ l ≤ 17	-19 ≤ h ≤ 19 -28 ≤ k ≤ 28 -14 ≤ l ≤ 14	-12 ≤ h ≤ 13 -23 ≤ k ≤ 28 -14 ≤ l ≤ 18	-20 ≤ h ≤ 20 -21 ≤ k ≤ 21 -25 ≤ l ≤ 25	-21 ≤ h ≤ 21 -22 ≤ k ≤ 22 -27 ≤ l ≤ 27	-22 ≤ h ≤ 22 -22 ≤ k ≤ 22 -27 ≤ l ≤ 26	-16 ≤ h ≤ 16 -19 ≤ k ≤ 17 -22 ≤ l ≤ 22
Reflections collected	4829	7414	3937	3690	19250	23731	24264	12955
Independent reflections	4099	6779	3391	3433	16094	21152	20317	10212
Completeness to θ_{max}	0.999	0.994	0.999	0.974	0.995	0.988	0.906	0.937
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Final R indices [$I>2\sigma_{(I)}$]	R_1 = 0.0461, wR_2 = 0.1160	R_1 = 0.0222, wR_2 = 0.0490	R_1 = 0.0400, wR_2 = 0.1050	R_1 = 0.0346, wR_2 = 0.0861	R_1 = 0.0303, wR_2 = 0.0678	R_1 = 0.0312, wR_2 = 0.0700	R_1 = 0.0286, wR_2 = 0.0676	R_1 = 0.0575, wR_2 = 0.1255
R indices (all data)	R_1 = 0.0531, wR_2 = 0.1208	R_1 = 0.0267, wR_2 = 0.0504	R_1 = 0.0447, wR_2 = 0.1073	R_1 = 0.0375, wR_2 = 0.0884	R_1 = 0.0413, wR_2 = 0.0739	R_1 = 0.0379, wR_2 = 0.0757	R_1 = 0.0387, wR_2 = 0.0736	R_1 = 0.0741, wR_2 = 0.1333

Table S1 (continuation). Crystal data and structure refinement for **$(Tp_2Ln)_2pPhd$ (3Ln)** and **$(Tp_2Ln)_2mPhd$ (4Ln)**

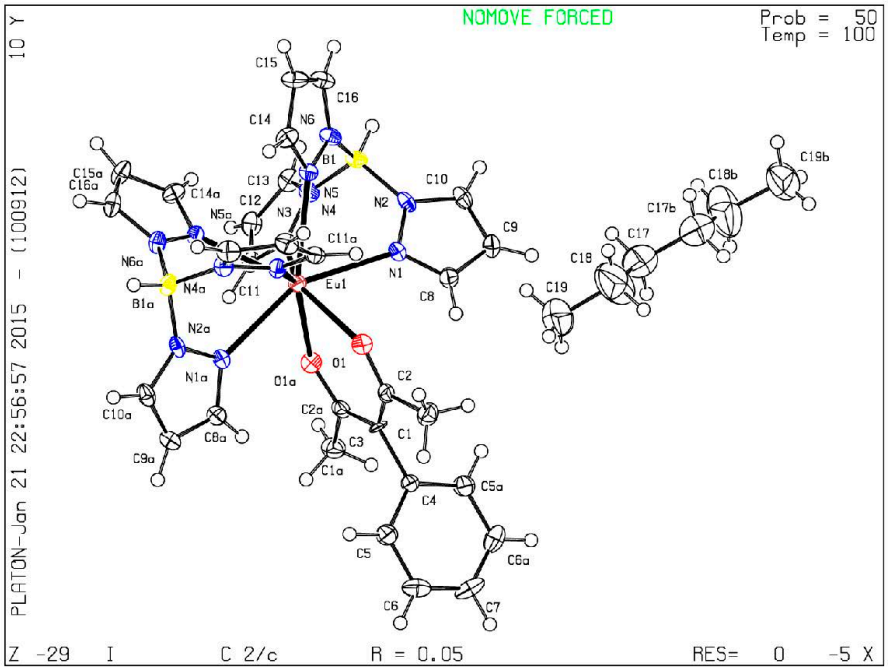
Compound	**3Eu·2 CH_2Cl_2**	**3Gd·3 C_7H_8**	**3Tb·3 C_7H_8**	**3Dy· 3 C_7H_8**	**4Eu·1.5 C_7H_8**	**4Gd· C_7H_{14} x solvent**	**4Tb·1.5 C_7H**	**4Dy·1.5 C_7H_8**
Empirical formula	$C_{54}H_{60}B_4Cl_4Eu_2N_{24}O_4$	$C_{73}H_{80}B_4Gd_2N_{24}$ O_4	$C_{73}H_{80}B_4N_{24}O_4Tb_2$	$C_{73}H_{80}B_4Dy_2N_{24}O_4$	$C_{125}H_{136}B_8N_{48}O_8Eu_4$	$C_{59}H_{70}B_4Gd_2N_{24}O_4$	$C_{125}H_{136}B_8N_{48}O_8Tb_4$	$C_{125}H_{136}B_8Dy_4N_{48}O_8$
Moiety formula	$C_{52}H_{56}B_4Eu_2N_{24}O_4$, $2(CH_2Cl_2)$	$C_{52}H_{56}B_4Gd_2N_{24}O_4$, $3(C_7H_8)$	$C_{52}H_{56}B_4N_{24}O_4Tb_2$, $3(C_7H_8)$	$C_{52}H_{56}B_4Dy_2N_{24}O_4$, $3(C_7H_8)$	$2(C_{52}H_{56}B_4N_{24}O_4Eu_2)$, $3(C_7H_8)$	$C_{52}H_{56}B_4Gd_2N_{24}O_4$, C_7H_{14}	$2(C_{52}H_{56}B_4N_{24}O_4Tb_2)$, $3(C_7H_8)$	$2(C_{52}H_{56}B_4Dy_2N_{24}O_4)$, $3(C_7H_8)$
Formula weight	1598.22	1715.35	1718.69	1725.85	3133.13	1537.13	3161.03	3175.29
Temperature	100(2)	150(2)	150(2)	100(2)	150(2)	150(2)	100(2)	100(2)
Wavelength	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	C2/c	C2/c	C2/c	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions	a = 18.094(3) Å b = 7.9885(12) Å c = 22.585(4) Å α = 90 ° β = 100.683(3) ° γ = 90 °	a = 33.4373(13) Å b = 16.0652(6) Å c = 14.8800(6) Å α = 90 ° β = 90.6487(14) ° γ = 90 °	a = 33.3788(8) Å b = 16.0649(5) Å c = 14.8904(4) Å α = 90 ° β = 90.8372(11) ° γ = 90 °	a = 33.2419(15)Å b = 16.0002(7)Å c = 14.8630(7)Å α = 90 ° β = 90.9174(18)° γ = 90 °	a = 7.8229(5) Å b = 29.326(2) Å c = 30.5001(17) Å α = 90 ° β = 95.385(3)° γ = 90 °	a = 15.4419(6) Å b = 15.4442(6) Å c = 16.9108(7) Å α = 75.8661(14) ° β = 79.6313(14) ° γ = 74.4742(12) °	a = 15.3419(6) Å b = 15.4724(6) Å c = 17.5268(8)Å α = 110.858(2) ° β = 103.635(2)° γ = 105.523(2)°	a = 7.8020(2)Å b = 29.0926(8)Å c = 30.3533(8)Å α = 90° β = 95.2817(11)° γ = 90°
Volume, $Å^3$	3208.0(9)	7992.7(5)	7983.8(4)	7904.3(6)	6966.3(8)	3739.8(3)	3483.6(3)	6860.4(3)
Z	2	4	4	4	2	2	1	2
Density (calcd.), g/cm^3	1.655	1.426	1.430	1.450	1.494	1.365	1.507	1.537
Absorption coefficient, mm^{-1}	2.169	1.707	1.820	1.939	1.848	1.816	2.078	12.046
F(000)	1596	3464	3472	3480	3156	1544	1586	3180
Crystal size, mm	0.23 × 0.05 × 0.04	0.490 × 0.192 × 0.100	0.280 × 0.140 × 0.188	0.31 × 0.26 × 0.11	0.55 × 0.03 × 0.02	0.488 × 0.071 × 0.056	0.21 × 0.17 × 0.14	0.50 × 0.05 × 0.04
Theta range for data collection	1.145 to 30.572	2.882 to 30.574	3.069 to 33.185	2.826 to 36.400	2.445 to 28.343	3.230 to 35.233	2.332 to 25.681	2.108 to 79.937
Index ranges	-25 ≤ h ≤ 20 -11 ≤ k ≤ 7 -32 ≤ l ≤ 31	-47 ≤ h ≤ 47 -22 ≤ k ≤ 22 -21 ≤ l ≤ 21	-35 ≤ h ≤ 51 -24 ≤ k ≤ 18 -22 ≤ l ≤ 22	-54 ≤ h ≤ 52 -25 ≤ k ≤ 25 -24 ≤ l ≤ 17	-10 ≤ h ≤ 7 -39 ≤ k ≤ 35 -40 ≤ l ≤ 39	-19 ≤ h ≤ 24 -19 ≤ k ≤ 24 -26 ≤ l ≤ 26	-18 ≤ h ≤ 18 -18 ≤ k ≤ 18 -21 ≤ l ≤ 21	-9 ≤ h ≤ 9 -36 ≤ k ≤ 37 -31 ≤ l ≤ 38
Reflections collected	9502	12246	14515	18428	17067	26980	13206	14468
Independent reflections	5712	11440	10581	13921	11782	19022	10510	12960
Completeness to θ_{max}	0.964	0.998	0.949	0.956	0.980	0.805	0.998	0.969
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Final R indices [$I>2\sigma_{(I)}$]	R_1 = 0.0443, wR_2 = 0.0854	R_1 = 0.0175, wR_2 = 0.0412	R_1 = 0.0383, wR_2 = 0.0748	R_1 = 0.0338, wR_2 = 0.0579	R_1 = 0.0451, wR_2 = 0.0928	R_1 = 0.0418, wR_2 = 0.0948	R_1 = 0.0338, wR_2 = 0.0579	R_1 = 0.0379, wR_2 = 0.0870
R indices (all data)	R_1 = 0.0928, wR_2 = 0.1008	R_1 = 0.0197, wR_2 = 0.0424	R_1 = 0.0686, wR_2 = 0.0849	R_1 = 0.0596, wR_2 = 0.0639	R_1 = 0.0806, wR_2 = 0.1079	R_1 = 0.0673, wR_2 = 0.1070	R_1 = 0.0596, wR_2 = 0.0639	R_1 = 0.0433, wR_2 = 0.0894

Table S1 (continuation). Crystal data and structure refinement for **$(Tp_2Ln)_3Pht$ (5Ln)**

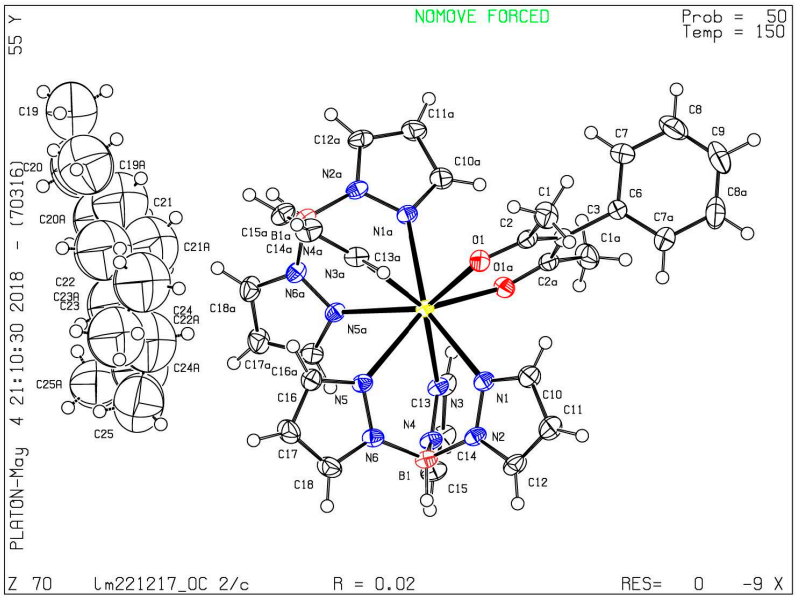
Compound	**5Eu·C_7H_8**	**5Gd·C_7H_8**	**5Tb·0.402 CH_2Cl_2·0.672 H_2O**	**5Dy·4C_7H_8·0.5C_7H_{16}**
Empirical formula	$C_{82}H_{89}B_6Eu_3N_{36}O_6$	$C_{82}H_{89}B_6Gd_3N_{36}O_6$	$C_{25.134}H_{27.716}B_2Cl_{0.268}N_{12}O_{2.224}Tb$	$C_{213}H_{242}B_{12}Dy_6N_{72}O_{12}$
Moiety formula	$C_{75}H_{81}B_6Eu_3N_{36}O_6$, C_7H_8	$C_{75}H_{81}B_6Gd_3N_{36}O_6$, C_7H_8	$C_{25}H_{27}B_2N_{12}O_2Tb$, 0.134($CH_2Cl_2$), 0.112($H_4O_2$)	2($C_{75}H_{81}B_6Dy_3N_{36}O_6$), 8($C_7H_8$), C_7H_{16}
Formula weight	2195.63	2211.50	723.55	5107.52
Temperature	150(2)	150(2)	100(2)	100(2)
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal system	Trigonal	Trigonal	Hexagonal	Triclinic
Space group	$R\bar{3}c$	$R\bar{3}c$	$P6_3/m$	$P\bar{1}$
Unit cell dimensions	a = 23.4251(11)Å b = 23.4251(11)Å c = 29.7290(18)Å α = 90° β = 90° γ = 120°	a = 23.3920(11)Å b = 23.3920(11)Å c = 29.8357(14)Å α = 90° β = 90° γ = 120°	a = 19.810(3) Å b = 19.810(3) Å c = 13.4702(19) Å α = 90° β = 90° γ = 120°	a = 15.2024(7) Å b = 20.4812(9) Å c = 21.8182(10) Å α = 108.6234(18)° β = 108.881(2)° γ = 95.255(2)°
Volume, $Å^3$	14127.8(16)	14138.4(15)	4578.2(14)	5945.6(5)
Z	6	6	6	1
Density (calcd.), g/cm^3	1.548	1.558	1.575	1.426
Absorption coefficient, mm^{-1}	2.044	2.157	2.386	10.463
F(000)	6600	6618	2159.2	2576
Crystal size, mm	0.12 × 0.09 × 0.08	0.17 × 0.13 × 0.09	0.19 × 0.05 × 0.03	0.323 × 0.261 × 0.050
Theta range for data collection	2.431 to 28.300	2.990 to 27.101	2.374 to 30.528	4.004 to 80.112
Index ranges	-26 ≤ h ≤ 29 -29 ≤ k ≤ 33 -27 ≤ l ≤ 39	-29 ≤ h ≤ 27 -29 ≤ k ≤ 29 -38 ≤ l ≤ 38	-17 ≤ h ≤ 27 -28 ≤ k ≤ 28 -18 ≤ l ≤ 18	-19 ≤ h ≤ 19 -25 ≤ k ≤ 26 -27 ≤ l ≤ 27
Reflections collected	3769	3480	4823	23945
Independent reflections	2999	3078	3651	20040
Completeness to θ_{max}	0.962	0.998	0.994	0.921
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
Final R indices [$I>2\sigma_{(I)}$]	R_1 = 0.0341, wR_2 = 0.0613	R_1 = 0.0333, wR_2 = 0.0666	R_1 = 0.0370, wR_2 = 0.0708	R_1 = 0.0442, wR_2 = 0.1075
R indices (all data)	R_1 = 0.0529, wR_2 = 0.0682	R_1 = 0.0399, wR_2 = 0.0713	R_1 = 0.0644, wR_2 = 0.0787	R_1 = 0.0562, wR_2 = 0.1152

Crystal structure refinement and ORTEP diagrams

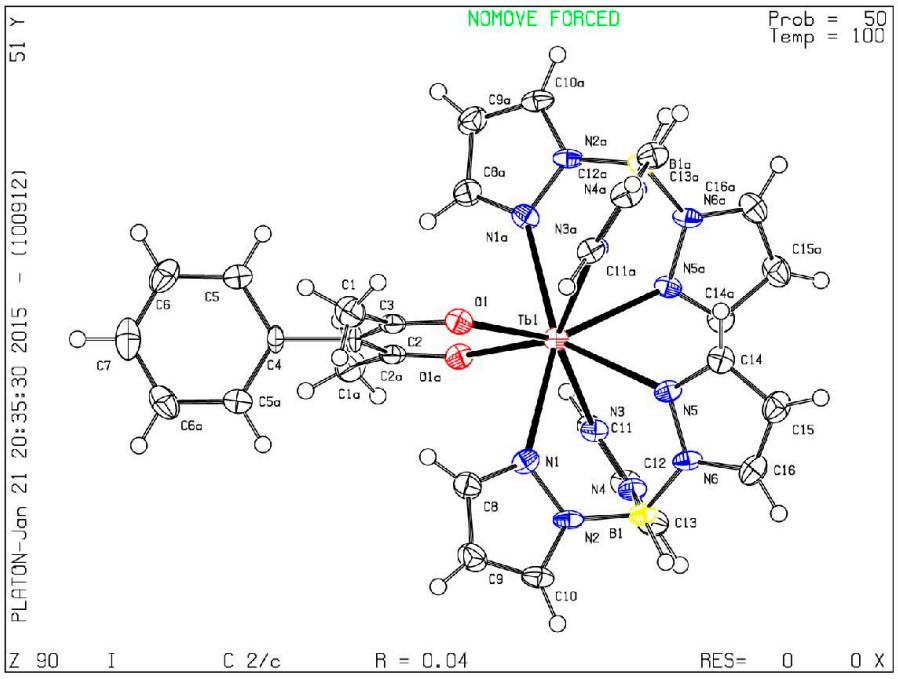
1Eu. The structure contains small voids. No interpretable electron density was found in the solvent-accessible voids and the cif and fcf files were thus corrected with reverse Fourier transform methods using the SQUEEZE routine [11] as implemented in the program Platon (100M-Version 130713). The resultant files were used in the further refinement. (The FAB file with details of the Squeeze results is appended to this cif file).



1Gd. A solvent-filled channel is occupied by heptane molecules disordered around two inversion centers and a two fold axis. Two crystallographically independent heptane molecules were refined. Their sum was set to half a molecule. All C-C bond distances in the heptane molecules were restrained to a target value of 1.53(2) Å. All 1,3 distances in the heptane molecules were restrained to a target value of 2.50(2) Å. The two molecules were restrained to have similar geometries. Uij components of A DPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar, and atoms to be close to isotropic. Subject to these conditions the occupancy ratio refined to 0.305(5) to 0.195(5).

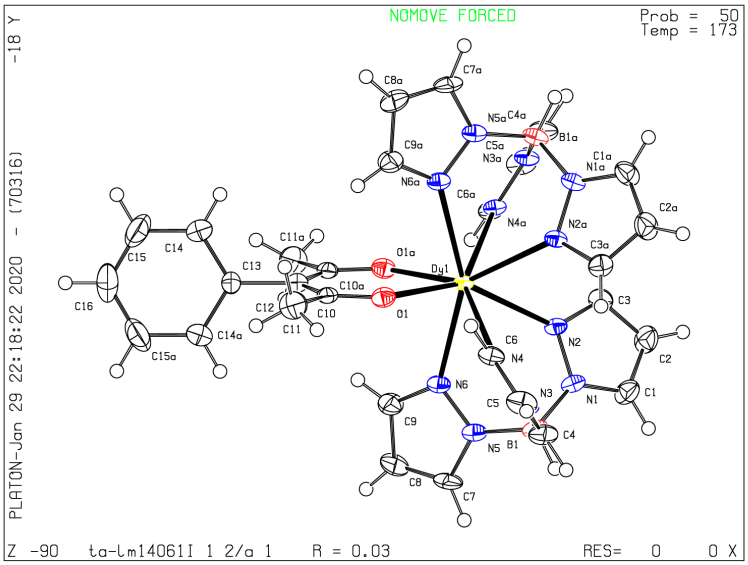


1Tb. The structure contains two symmetry-dependent solvent-accessible voids of 462 Å^3 each. No interpretable electron density was found in the solvent-accessible voids and the cif and fcf files were thus corrected using reverse Fourier transform methods with the SQUEEZE routine [11] as implemented in the program Platon (100M-Version 130713). The resultant files were used in the further refinement. (The FAB file with details of the Squeeze results is appended to this cif file). The Squeeze procedure corrected for 71 electrons within each of the solvent-accessible voids.



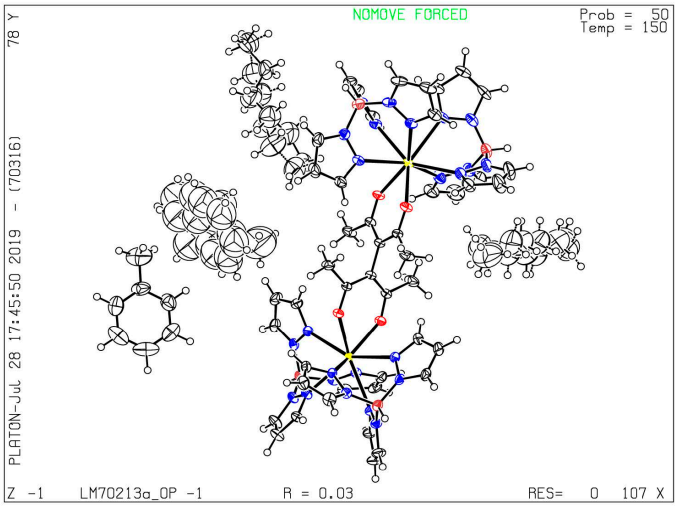
1Dy. The structure contains one independent molecule in the asymmetric unit and two symmetry-dependent solvent-accessible voids of 485 Å^3 each. No interpretable electron density was found in the solvent-accessible voids and the cif and fcf files were thus corrected using reverse Fourier transform methods with the MASK routine in Olex2.[12] The resultant files were used in the further

refinement. (The FAB file with details of the MASK results is appended to this cif file). The MASK procedure corrected for 117 electrons within each of the solvent-accessible voids.

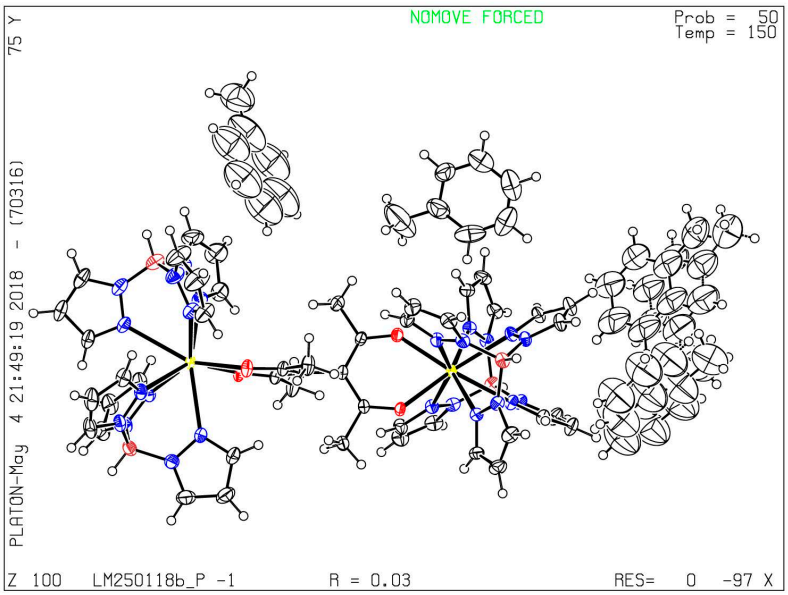


2Eu. Two hexane molecules are disordered over each of two positions, one in a general position, the other located on an inversion center (but with both moieties being exactly centrosymmetric). All disordered moieties were restrained to have similar geometries using a combination of Shelxl SAME and SADI commands. C-C bond lengths in hexane molecules were restrained to target values. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.539(7) to 0.461(7) for the molecule in the general position, and to 0.427(8) to 0.573(8) for the other hexane molecule.

A toluene molecule was refined as partially occupied and disordered over two moieties. Both disordered moieties were ill-defined and were restrained to have geometries similar to another non-disordered toluene molecule. Their aromatic rings were constrained to resemble ideal hexagons with C-C bond distances of 1.39 Å. The molecules were restrained to be close to planar and their atoms to be close to isotropic. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy rates refined to 0.427(8) to 0.422(9). Additional electron density associated with this solvation region was too ill defined for additional disorder refinement.



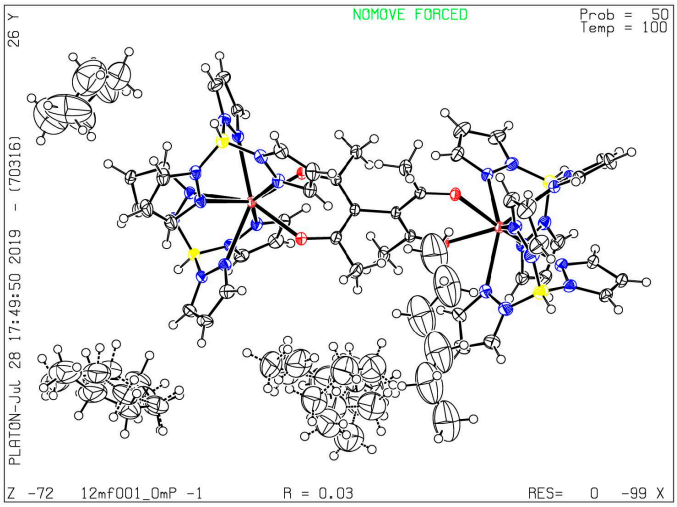
2Gd. Three toluene molecules are disordered, one around an inversion center, two in a general position. All disordered toluene molecules were restrained to have a similar geometry as another fourth, not disordered toluene molecule. The minor moiety of C57 to C63 and both moieties of C64 to C70 were each restrained to be close to planar. In the inversion-disordered molecule, the C-ortho to C-methyl distances were restrained to be similar. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratios refined to 0.799(6) to 0.201(6) (C57 to C63), and 0.707(6) to 0.293(6) (C64-C70).



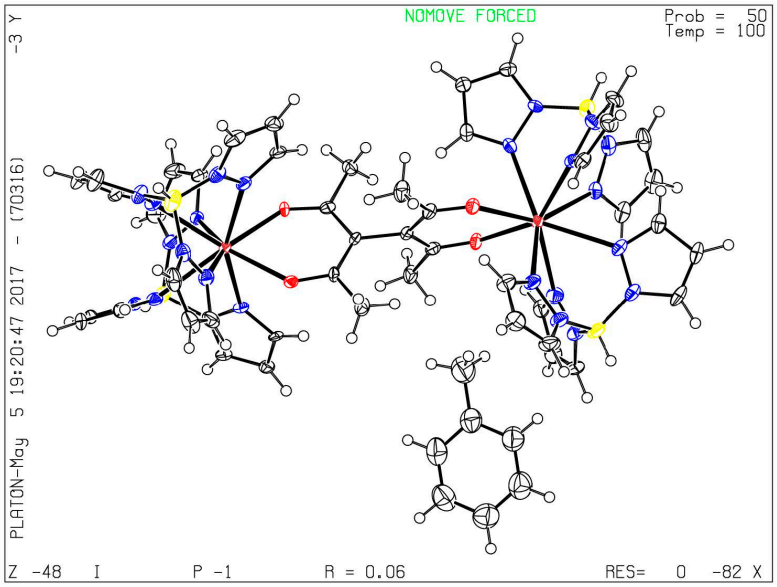
2Tb. A hexane molecule is disordered across an inversion center. A methylcylcopentane molecule is disordered by inversion, and a third solvent occupied site was refined as disordered among two cyclopentane and one hexane moieties.

Hexane bond distances and C-CH_3 distances of methyl cylcopentane were restrained to target values (1.55(2) and 1.53(2) Å respectively). Equivalent disordered moieties were restrained to have similar geometries. ADPs of methyl atoms related by inversion symmetry were constrained to be identical. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained

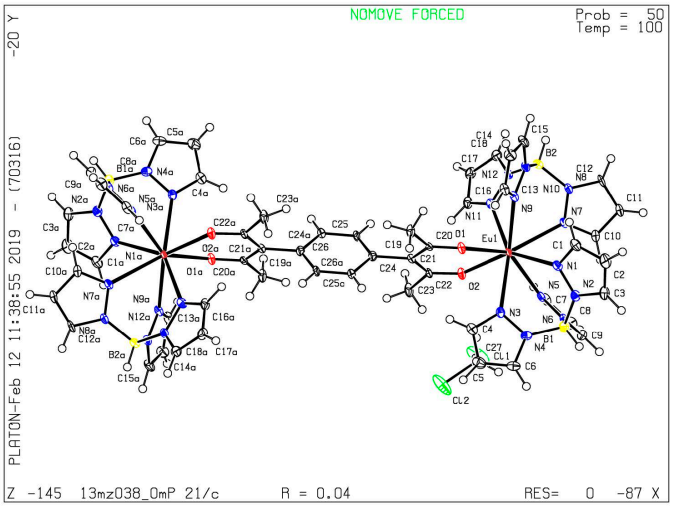
to be similar. Subject to these conditions the occupancy ratio refined to 0.534(9) to 0.466(9) for the methyl cylcopentane molecule and occupancies refined to 0.342(6), 0.250(6) and 0.420(6) for the two methyl cylcopentane and hexane moieties.



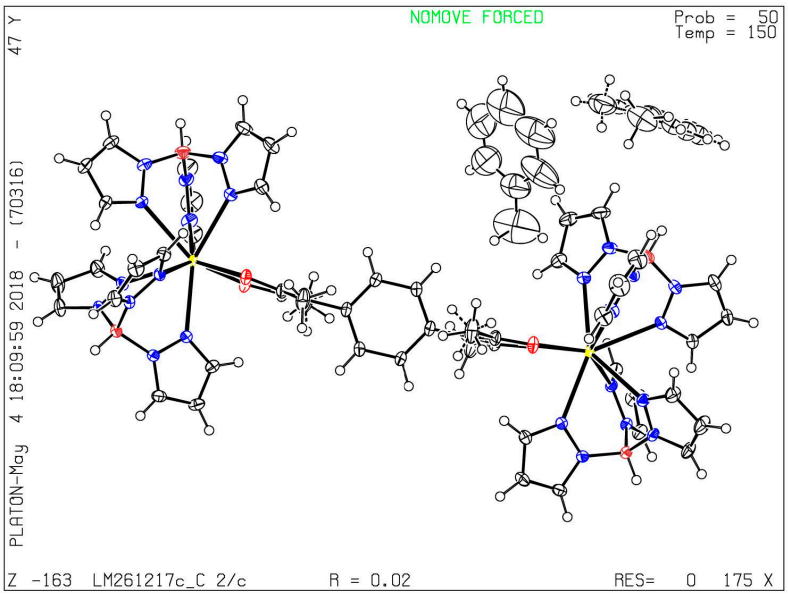
2Dy.



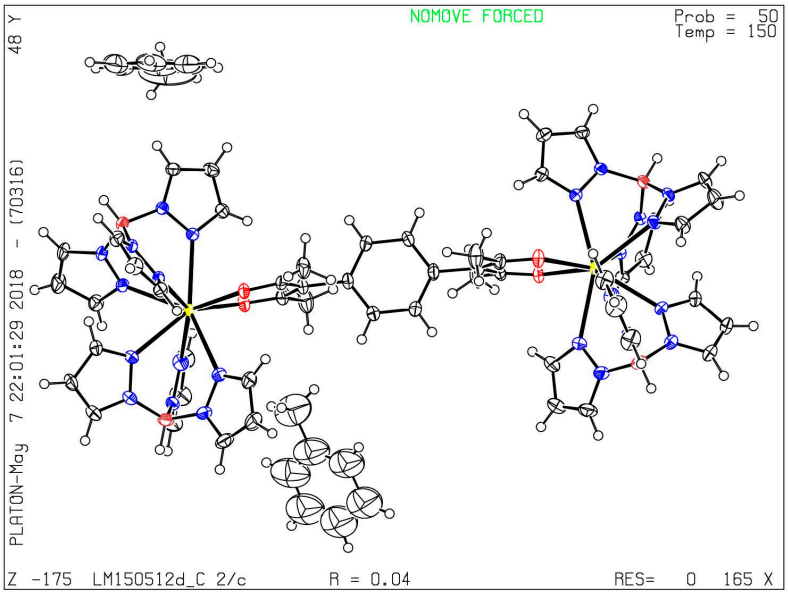
3Eu.



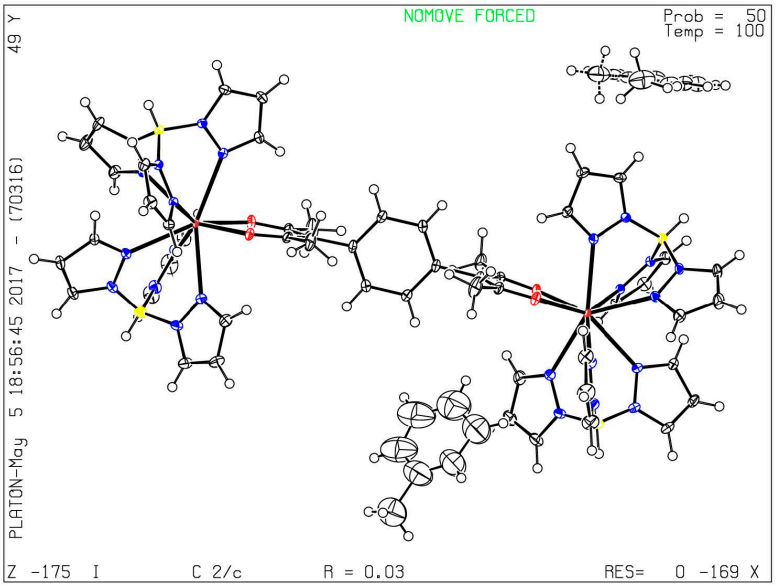
3Gd. Two toluene molecules are disordered, one around an inversion center, the other in a general position. The benzene ring of the former was constrained to resemble an ideal hexagon with C-C bond distances of 1.39 Angstrom. For the latter, the two disordered moieties were restrained to have similar geometries. In all toluene molecules, the C-ortho to C-methyl distances were restrained to be similar. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio for the toluene molecule in the general position refined to 0.42(3) to 0.58(3).



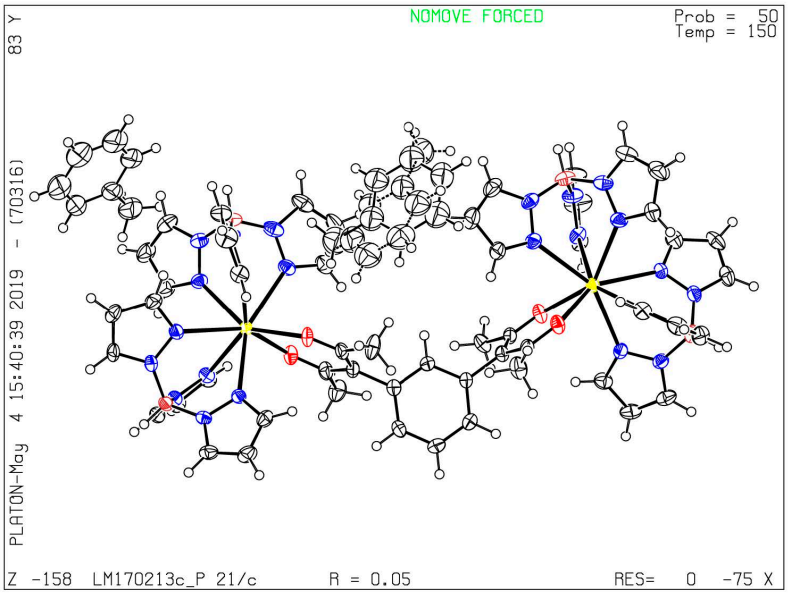
3Tb. A toluene molecule is disordered around an inversion center. It was restrained to have a similar geometry as another toluene molecule in a general position. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar.



3Dy. A toluene is disordered around an inversion center and a second toluene is disordered in a general position. All three toluene moieties were restrained to have similar geometries, and Uij components of ADPs were restrained to be similar for atoms closer to each other than 1.7 Å. The occupancy rate for the second toluene molecule refined to 0.816(4) to 0.184(4).

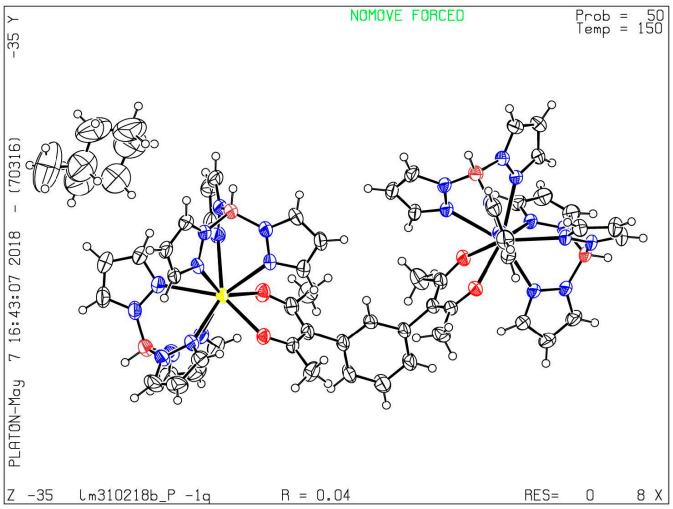


4Eu. Two toluene molecules are disordered. One in a general position, and the other is located atop an inversion center. The benzene rings of the molecule in the general position were constrained to resemble an ideal hexagon with C-C bond distances of 1.39 Å. All three disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio for the moleucle in the general position refined to 0.514(6) to 0.514(6).



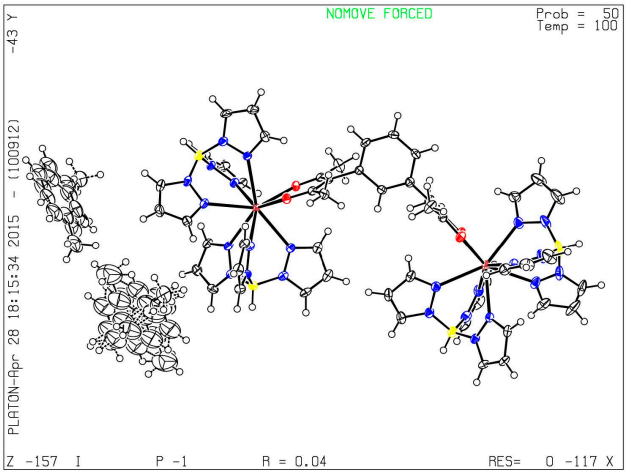
4Gd. The CH_2-CH_2 bonds of an ill-defined methylcyclohexane molecule were restrained to be similar to each other. The C-CH_3 bond length was restrained to a target value of 1.53(2) Å, and the C(ortho) to C(methyl) distances were restrained to be similar. ADPs were subjected to a rigid bond restraint.

The structure contains solvent accessible channels of 533 $Å^3$ combined. The residual electron density in these channels is highly disordered and no model could be developed that is commensurate with the known solvents present (methylcyclohexane, heptane and methylene chloride). The res and hkl files were instead corrected with reverse Fourier transform methods using the SQUEEZE routine [10] as implemented in the program Platon. The resultant files were used in the further refinement. (The FAB file with details of the Squeeze results is appended to this cif file). The Squeeze procedure corrected for 130 electrons within the solvent accessible voids.

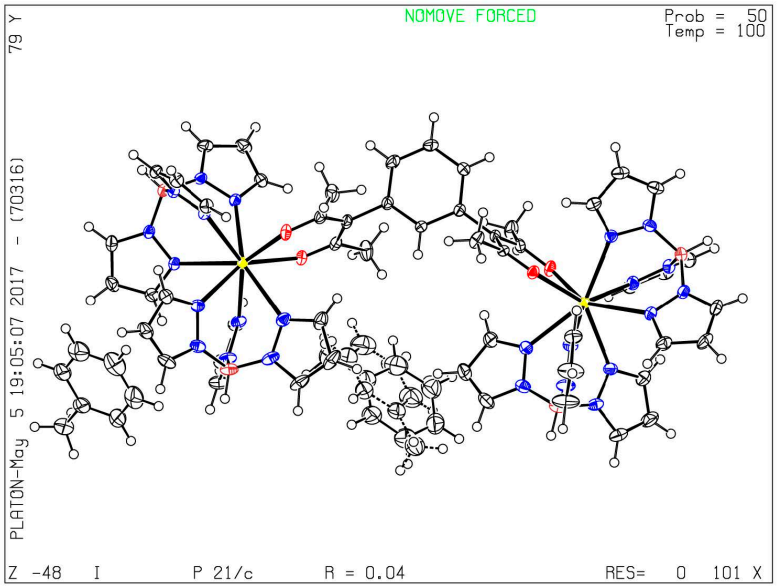


4Tb. Two interstitial sites are occupied by disordered toluene molecules. One site, in a general position, was refined as harbouring two moieties with different orientations of the methyl group. The second site also features two molecule orientations, but each unit is in addition disordered around a

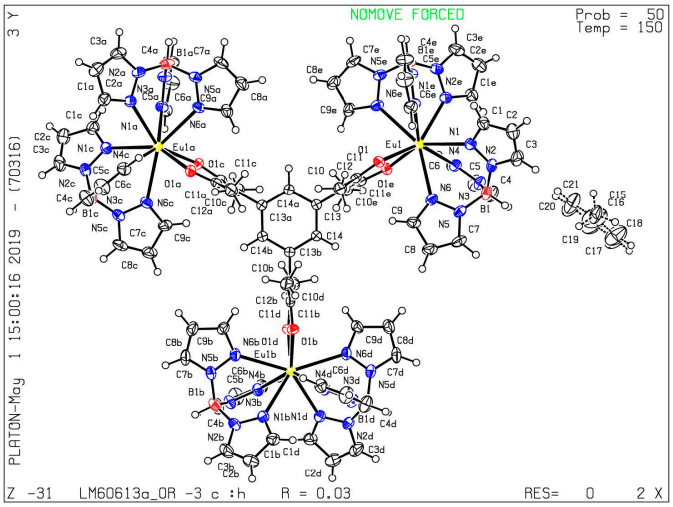
crystallographic inversion center. The phenyl rings of all toluene molecules were constrained to resemble ideal hexagons with C-C distances of 1.39 Å. The methyl C atoms were restrained to have similar 1,2 and 1,3 distances, and to lie within one plane with the phenyl rings for the second site. Uij components of ADPs of disordered atoms were restrained to be similar if closer than 1.7 Å (SIMU), and were subjected to a rigid bond restraint (RIGU). A weak anti-bumping restraint was applied to keep disordered atoms from approaching too closely to the main molecule.



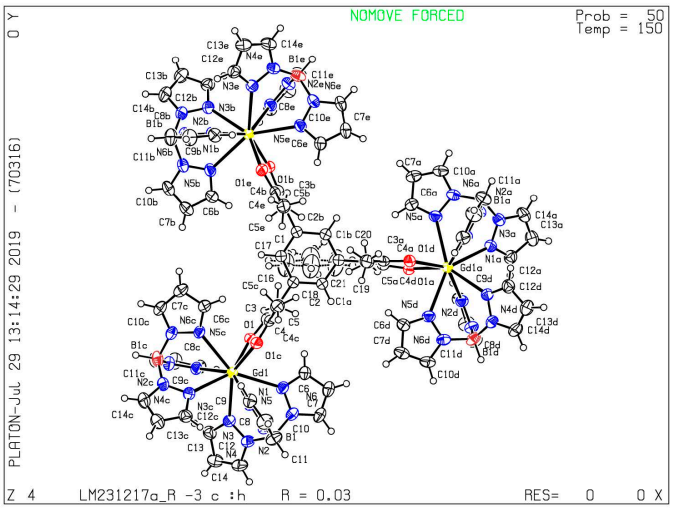
4Dy. A toluene is disordered around an inversion center and a second toluene is disordered in a general position. All three toluene moieties were restrained to have similar geometries, and Uij components of ADPs were restrained to be similar for atoms closer to each other than 1.7 Å. The occupancy rate for the second toluene molecule refined to 0.521(5) to 0.479(5).



5Eu. The toluene molecule was refined as disordered on a three fold rotoinversion axis with 1/6 occupancy for the symmetry-independent moieties. All thermal parameters were restrained to be similar to each other. The phenyl ring was constrained to have ideal distances and angles. The methyl group was restrained to be in the same plane as the phenyl ring with similar distances from C21 and C15. The thermal parameter of C15 was restrained to be more isotropic.

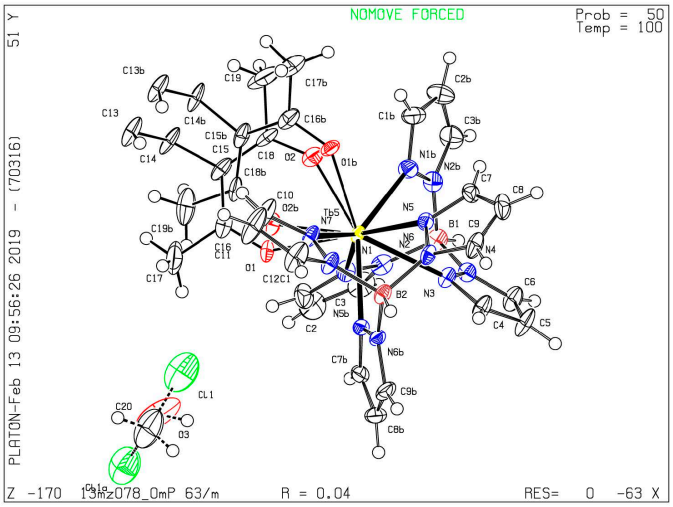


5Gd. A toluene molecule is disordered around a six-fold rotoinversion axis, split over six symmetry-equivalent positions. The benzene ring was constrained to resemble an ideal hexagon with 1.39 Å C-C bond distances (AFIX 66). The C-C(methyl) bond distance was restrained to a target value of 1.56(2) Å (DFIX), and the methyl C-atom was restrained to be in plane with the phenyl ring C atoms (FLAT). Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar (SIMU 0.01).



5Tb. The Pht ligand is disordered over two positions created from each other by a crystallographic inversion center. It is also bisected by a threefold rotation axis. Due to correlation between disordered atoms, bond distance and angle restraints were applied. All chemically equivalent bonds and 1,3 distances in the disordered moiety were restrained to be the same within 0.02 Å. Neighboring atoms were restrained to have ADPs with similar Uij components (SIMU command in Shextl), and to be approximately isotropic. The benzene ring bound carbon atom was restrained to be in plane with the next three C atoms of the six membered ring. A partially occupied solvation site is present. It was refined to be occupied by methylene chloride and water. The C-Cl distances were restrained to be 1.70(2) Å, with the C atom located on a crystallographic mirror plane. The C and Cl atom were restrained to have ADPs with similar Uij components (SIMU command in Shextl). The

water molecule was refined as disordered across the mirror plane close to the position of the methylene chloride C atom. Reflections 0 1 1, 0 1 0 and 0 0 2 were obstructed by the beam stop and were omitted from the refinement.



5Dy. Three toluene molecules were refined as disordered in general positions with each in two alternative orientations. All toluene moieties were restrained to have similar geometries as a fourth, not disordered toluene molecule. One toluene moiety was restrained to be planar. A heptane molecule is disordered around an inversion center: C-C(methyl) bonds were restrained to 1.54(2) Angstroms. All other heptane C-C bonds were restrained to be similar to each other. Uij components of ADPs of disordered atoms were restrained to be similar for atoms closer to each other than 1.7 Å. The occupancy ratios for the three disordered toluene molecules refined to 0.681(7) to 0.319(7), 0.521(10) to 0.479(1), and 0.557(9) to 0.443(9).

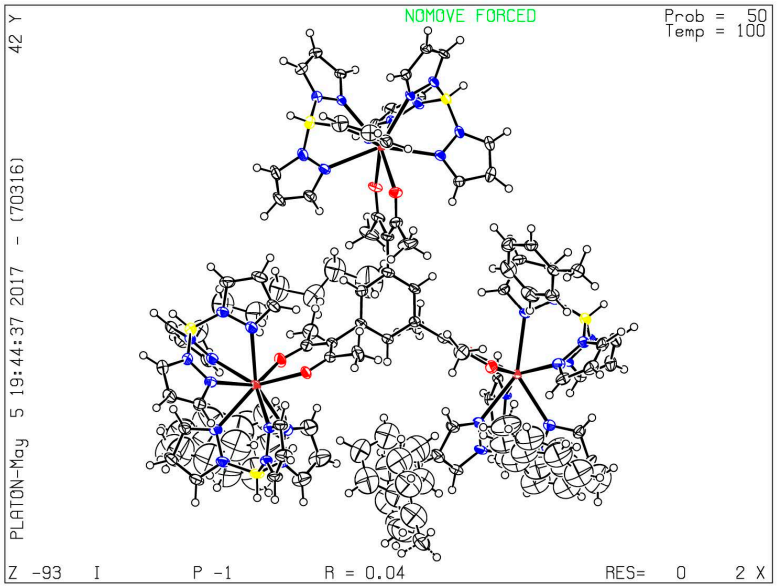


Table S2. Selected bond distances, angles and weak intemolecular contacts for the complexes studied.

1Eu			
Selected bond distances, Å			
Eu1-O1	2.304(2)	Eu1-N1	2.575(3)
Eu1-N3	2.510(3)	Eu1-N5	2.591(3)
Selected angles, º			
N1-Eu1-N1	154.10(14)	N5-Eu1-N5	70.55(14)
N1-Eu1-N5	71.03(10)	O1-Eu1-N1	83.80(10)
N1-Eu1-N5	133.72(10)	O1-Eu1-N1	75.39(10)
N3-Eu1-N1	71.10(10)	O1-Eu1-N3	75.76(9)
N3-Eu1-N1	117.14(10)	O1-Eu1-N3	136.05(9)
N3-Eu1-N3	145.69(13)	O1-Eu1-N5	147.26(10)
N3-Eu1-N5	76.46(10)	O1-Eu1-N5	118.08(9)
N3-Eu1-N5	75.67(10)	O1-Eu1-O1	73.07(12)
Weak intemolecular contacts, Å			
C7-C10	3.283	C18-H18B	2.759
C11-H6	2.866	H18B-H18B	1.980
H11-C14	2.898		
1Gd			
Selected bond distances, Å			
Gd1-O1	2.2963(10)	Gd1-N1	2.5657(11)
Gd1-N3	2.4941(11)	Gd1-N5	2.5751(11)
Selected angles, º			
N1-Gd1-N1	154.52(5)	N5-Gd1-N5	70.49(5)
N1-Gd1-N5	133.59(4)	O1-Gd1-N1	74.72(4)
N1-Gd1-N5	70.77(4)	O1-Gd1-N1	84.82(4)
N3-Gd1-N1	116.41(4)	O1-Gd1-N3	135.59(4)
N3-Gd1-N1	71.54(4)	O1-Gd1-N3	75.66(4)
N3-Gd1-N3	146.19(5)	O1-Gd1-N5	117.65(4)
N3-Gd1-N5	75.64(4)	O1-Gd1-N5	147.83(4)
N3-Gd1-N5	76.88(4)	O1-Gd1-O1	73.30(5)
Weak intemolecular contacts, Å			
C9-C12	3.325	C25-H21B	2.837
H13-C16	2.842	H25C-H25C	1.997
C15-H19C	2.749	H25C-C22	1.726
H17-H25A	2.354	H25C-C20	2.535
H17-H20A	2.322	H25C-H20A	2.333
H18-H25B	2.283	H25C-C21	1.748
C11-H20B	2.819	H25C-H21A	2.086
H11-H20B	2.331	H25C-H22A	1.02
H19B-H25B	2.162	H25C-H22B	1.748
C20-H25A	2.203	H25C-C19	2.733
C20-H25B	2.781	H25C-H19B	2.315
H20A-H25A	1.95	H25C-H21B	2.361
H20B-H25A	2.194	C22-C22	1.399
C21-H25A	2.153	C22-C23	2.827
C21-H25B	1.826	C22-C20	2.546
H21A-H25A	2.075	C22-H20A	2.546
H21A-H25B	1.275	C22-C21	1.457
C22-H25A	2.244	C22-H21A	1.991
C22-H25B	1.865	C22-H21B	1.993
H22A-H25A	2.296	C22-H22A	0.992

H22B-H25A	2.178	C22-H22B	0.99
H22B-H25B	2.388	C22-H24A	2.534
C23-H24A	2.343	C22-C19	2.327
C23-H24B	2.158	C22-H19B	2.144
C23-H25A	2.252	C22-H19C	2.9
C23-H25B	1.525	C22-H20B	2.544
C23-C19	2.651	C23-C21	2.538
C23-H19A	2.61	C23-H21A	2.497
C23-H19B	1.965	C23-H22A	2.046
C23-C20	3.348	C23-H22B	2.046
H23A-H24A	1.985	C23-H19C	2.802
H23A-H24B	1.24	C23-H20A	2.027
H23A-H25A	2.2	C23-H21B	2.695
H23A-H25B	2.136	H23A-H22A	2.138
H23A-C19	1.969	H23A-C20	2.802
H23A-H19A	2.096	H23A-H20A	2.25
H23A-H19B	1.17	H23B-C21	2.53
H23B-H24A	1.897	H23B-H21A	2.109
H23B-H24B	2.398	C24-H22B	2.445
H23B-H25A	2.032	C24-H24A	0.988
H23B-H25B	0.885	C24-H24B	0.992
H23B-C19	2.534	C24-H25A	2.07
H23B-H19A	2.268	C24-C19	1.149
H23B-H19B	2.188	C24-H19A	1.187
C24-H25B	2.725	C24-H19C	2
C24-H19B	2.636	C24-C20	2.149
C25-H25C	2.831	C24-H20A	2.183
C25-C22	2.417	C24-H20B	2.839
C25-C20	2.645	C24-C21	3.183
C25-H20A	2.519	C25-H24A	2.069
C25-H20B	2.823	C25-H24B	2.068
C25-C21	1.992	C25-H25A	0.979
C25-H21A	1.875	C25-H25B	0.981
C25-H22A	1.954	C25-H19A	2.07
C25-H22B	2.549	H25C-H24B	2.369
C25-C19	3.146	H25C-H25A	1.6
C25-H19B	2.447	H25C-H25B	1.6
C9-C12	3.325	C25-H21B	2.837
H13-C16	2.842	H25C-H25C	1.997
C15-H19C	2.749	H25C-C22	1.726
H17-H25A	2.354	H25C-C20	2.535
H17-H20A	2.322	H25C-H20A	2.333
H18-H25B	2.283	H25C-C21	1.748
C11-H20B	2.819	H25C-H21A	2.086
H11-H20B	2.331	H25C-H22A	1.02
H19B-H25B	2.162	H25C-H22B	1.748
C20-H25A	2.203	H25C-C19	2.733
C20-H25B	2.781	H25C-H19B	2.315
H20A-H25A	1.95	H25C-H21B	2.361
H20B-H25A	2.194	C22-C22	1.399
C21-H25A	2.153	C22-C23	2.827
C21-H25B	1.826	C22-C20	2.546

H21A-H25A	2.075	C22-H20A	2.546
H21A-H25B	1.275	C22-C21	1.457
C22-H25A	2.244	C22-H21A	1.991
C22-H25B	1.865	C22-H21B	1.993
H22A-H25A	2.296	C22-H22A	0.992
H22B-H25A	2.178	C22-H22B	0.99
H22B-H25B	2.388	C22-H24A	2.534
C23-H24A	2.343	C22-C19	2.327
C23-H24B	2.158	C22-H19B	2.144
C23-H25A	2.252	C22-H19C	2.9
C23-H25B	1.525	C22-H20B	2.544
C23-C19	2.651	C23-C21	2.538
C23-H19A	2.61	C23-H21A	2.497
C23-H19B	1.965	C23-H22A	2.046
C23-C20	3.348	C23-H22B	2.046
H23A-H24A	1.985	C23-H19C	2.802
H23A-H24B	1.24	C23-H20A	2.027
H23A-H25A	2.2	C23-H21B	2.695
H23A-H25B	2.136	H23A-H22A	2.138
H23A-C19	1.969	H23A-C20	2.802
H23A-H19A	2.096	H23A-H20A	2.25
H23A-H19B	1.17	H23B-C21	2.53
H23B-H24A	1.897	H23B-H21A	2.109
H23B-H24B	2.398	C24-H22B	2.445
H23B-H25A	2.032	C24-H24A	0.988
H23B-H25B	0.885	C24-H24B	0.992
H23B-C19	2.534	C24-H25A	2.07
H23B-H19A	2.268	C24-C19	1.149
H23B-H19B	2.188	C24-H19A	1.187
C24-H25B	2.725	C24-H19C	2
C24-H19B	2.636	C24-C20	2.149
C25-H25C	2.831	C24-H20A	2.183
C25-C22	2.417	C24-H20B	2.839
C25-C20	2.645	C24-C21	3.183
C25-H20A	2.519	C25-H24A	2.069
C25-H20B	2.823	C25-H24B	2.068
C25-C21	1.992	C25-H25A	0.979
C25-H21A	1.875	C25-H25B	0.981
C25-H22A	1.954	C25-H19A	2.07
C25-H22B	2.549	H25C-H24B	2.369
C25-C19	3.146	H25C-H25A	1.6
C25-H19B	2.447	H25C-H25B	1.6
1Tb			
Selected bond distances, Å			
Tb1-O1	2.278(3)	Tb1-N1	2.559(3)
Tb1-N3	2.485(3)	Tb1-N5	2.571(3)
Selected angles, º			
N1-Tb1-N1	154.09(15)	N5-Tb1-N5	70.01(15)
N1-Tb1-N5	133.44(11)	O1-Tb1-N1	74.55(10)
N1-Tb1-N5	71.32(11)	O1-Tb1-N1	84.68(10)
N3-Tb1-N1	116.25(10)	O1-Tb1-N3	135.81(10)
N3-Tb1-N1	71.84(10)	O1-Tb1-N3	75.52(10)

N3-Tb1-N3	146.10(15)	O1-Tb1-N5	117.57(10)
N3-Tb1-N5	75.16(11)	O1-Tb1-N5	148.13(10)
N3-Tb1-N5	77.21(11)	O1-Tb1-O1	73.56(14)
Weak intemolecular contacts, Å			
C7-C10	3.317	H11-C14	2.842
C11-H6	2.885		
1Dy			
Selected bond distances, Å			
Dy1-O1	2.261(2)	Dy1-N6	2.540(3)
Dy1-N4	2.461(3)	Dy1-N2	2.545(3)
Selected angles, º			
N2-Dy1-N2	70.36(12)	N6-Dy1-N6	154.48(13)
N4-Dy1-N2	75.61(8)	O1-Dy1-N2	117.50(8)
N4-Dy1-N2	77.32(9)	O1-Dy1-N2	147.73(8)
N4-Dy1-N4	146.73(13)	O1-Dy1-N4	135.70(9)
N4-Dy1-N6	115.79(8)	O1-Dy1-N4	75.05(9)
N4-Dy1-N6	72.02(8)	O1-Dy1-N6	74.60(9)
N6-Dy1-N2	133.63(9)	O1-Dy1-N6	84.97(9)
N6-Dy1-N2	70.80(9)	O1-Dy1-O1	73.79(12)
Weak intemolecular contacts, Å			
C7-C16	3.341	C3-H6	2.844
2Eu			
Selected bond distances, Å			
Eu1-O1	2.2991(19)	Eu2-O3	2.3016(19)
Eu1-O2	2.3119(19)	Eu2-O4	2.3088(18)
Eu1-N12	2.488(2)	Eu2-N24	2.491(2)
Eu1-N4	2.515(3)	Eu2-N16	2.528(2)
Eu1-N10	2.522(2)	Eu2-N14	2.574(2)
Eu1-N2	2.554(3)	Eu2-N18	2.578(2)
Eu1-N8	2.586(2)	Eu2-N20	2.587(2)
Eu1-N6	2.656(2)	Eu2-N22	2.600(2)
Selected angles, º			
O1-Eu1-O2	71.68(7)	O3-Eu2-O4	72.17(7)
O1-Eu1-N12	141.94(8)	O3-Eu2-N24	136.14(7)
O2-Eu1-N12	84.06(7)	O4-Eu2-N24	75.96(7)
O1-Eu1-N4	73.06(8)	O3-Eu2-N16	77.50(7)
O2-Eu1-N4	125.56(8)	O4-Eu2-N16	135.93(7)
N12-Eu1-N4	143.93(8)	N24-Eu2-N16	144.61(7)
O1-Eu1-N10	105.42(7)	O3-Eu2-N14	148.32(7)
O2-Eu1-N10	147.65(8)	O4-Eu2-N14	118.65(7)
N12-Eu1-N10	79.81(8)	N24-Eu2-N14	74.40(7)
N4-Eu1-N10	81.52(9)	N16-Eu2-N14	75.38(7)
O1-Eu1-N2	101.38(8)	O3-Eu2-N18	85.57(7)
O2-Eu1-N2	74.46(8)	O4-Eu2-N18	73.45(7)
N12-Eu1-N2	99.69(9)	N24-Eu2-N18	113.25(7)
N4-Eu1-N2	73.46(9)	N16-Eu2-N18	73.03(7)
N10-Eu1-N2	135.79(8)	N14-Eu2-N18	71.11(7)
O1-Eu1-N8	75.65(7)	O3-Eu2-N20	75.41(7)
O2-Eu1-N8	78.89(7)	O4-Eu2-N20	83.36(7)
N12-Eu1-N8	71.11(8)	N24-Eu2-N20	71.65(7)
N4-Eu1-N8	129.11(8)	N16-Eu2-N20	118.98(7)

N10-Eu1-N8	69.42(8)	N14-Eu2-N20	132.85(7)
N2-Eu1-N8	152.62(8)	N18-Eu2-N20	153.67(7)
O1-Eu1-N6	146.82(8)	O3-Eu2-N22	117.30(7)
O2-Eu1-N6	130.82(7)	O4-Eu2-N22	146.95(7)
N12-Eu1-N6	70.80(8)	N24-Eu2-N22	77.20(7)
N4-Eu1-N6	73.76(8)	N16-Eu2-N22	75.98(7)
N10-Eu1-N6	68.94(8)	N14-Eu2-N22	71.24(7)
N2-Eu1-N6	69.33(8)	N18-Eu2-N22	135.89(7)
N8-Eu1-N6	127.16(8)	N20-Eu2-N22	70.08(7)
Weak intemolecular contacts, Å			
H29-C17	2.728	C27-H58A	2.748
N16-H27	2.747	H42-H55B	2.383
C18-H35	2.679	C14-H56B	2.824
C19-H35	2.900	H14-C54	2.838
H27-C34	2.793	H14-C56	2.846
N17-H45	2.667	H14-H56B	2.049
H16-C21	2.875	C10-C69	3.298
H23-C38	2.658	H10A-C69	2.890
H23-C39	2.871	H10B-C69	2.805
H24-C46	2.727	H10B-H69B	2.209
C23-H50	2.851	C44-H64	2.887
H32-C50	2.872	C53-H65	2.815
H5B-H59C	2.385	H53B-C65	2.770
C26-H58A	2.881	H53B-H65	2.096
2Gd			
Selected bond distances, Å			
Gd1-O3	2.2966(16)	Gd2-O1	2.2883(17)
Gd1-O4	2.2986(16)	Gd2-O2	2.3052(16)
Gd1-N17	2.4760(19)	Gd2-N10	2.464(2)
Gd1-N22	2.5169(19)	Gd2-N7	2.505(2)
Gd1-N24	2.562(2)	Gd2-N6	2.507(2)
Gd1-N20	2.5723(19)	Gd2-N1	2.538(2)
Gd1-N15	2.5801(19)	Gd2-N12	2.571(2)
Gd1-N13	2.585(2)	Gd2-N4	2.648(2)
Selected angles, º			
O3-Gd1-O4	72.70(6)	O1-Gd2-O2	71.88(6)
O3-Gd1-N17	136.58(6)	O1-Gd2-N10	142.84(7)
O4-Gd1-N17	75.41(6)	O2-Gd2-N10	84.30(7)
O3-Gd1-N22	76.91(6)	O1-Gd2-N7	104.11(6)
O4-Gd1-N22	136.13(6)	O2-Gd2-N7	146.27(7)
N17-Gd1-N22	144.91(6)	N10-Gd2-N7	80.16(7)
O3-Gd1-N24	85.42(6)	O1-Gd2-N6	72.82(7)
O4-Gd1-N24	73.57(6)	O2-Gd2-N6	125.01(7)
N17-Gd1-N24	112.78(6)	N10-Gd2-N6	143.50(7)
N22-Gd1-N24	73.16(6)	N7-Gd2-N6	82.87(8)
O3-Gd1-N20	147.76(6)	O1-Gd2-N1	102.52(7)
O4-Gd1-N20	118.92(6)	O2-Gd2-N1	74.14(7)
N17-Gd1-N20	74.55(6)	N10-Gd2-N1	97.64(8)
N22-Gd1-N20	75.26(6)	N7-Gd2-N1	137.42(7)
N24-Gd1-N20	71.22(6)	N6-Gd2-N1	74.04(8)
O3-Gd1-N15	116.56(6)	O1-Gd2-N12	75.64(7)
O4-Gd1-N15	146.25(6)	O2-Gd2-N12	76.98(7)

N17-Gd1-N15	77.63(6)	N10-Gd2-N12	71.38(7)
N22-Gd1-N15	76.30(6)	N7-Gd2-N12	69.74(7)
N24-Gd1-N15	136.71(6)	N6-Gd2-N12	131.10(8)
N20-Gd1-N15	71.84(7)	N1-Gd2-N12	150.00(7)
O3-Gd1-N13	75.32(6)	O1-Gd2-N4	146.13(7)
O4-Gd1-N13	82.70(6)	O2-Gd2-N4	131.92(6)
N17-Gd1-N13	72.06(6)	N10-Gd2-N4	70.47(7)
N22-Gd1-N13	119.11(6)	N7-Gd2-N4	69.54(7)
N24-Gd1-N13	153.06(6)	N6-Gd2-N4	73.37(7)
N20-Gd1-N13	133.32(6)	N1-Gd2-N4	69.77(7)
N15-Gd1-N13	69.87(6)	N12-Gd2-N4	127.63(7)
Weak intermolecular contacts, Å			
H43-C7	2.766	H11-C32	2.748
N22-H14	2.679	H12-C38	2.654
C8-H44	2.682	C12-H54	2.839
H14-C49	2.750	H34-C55	2.875
N23-H33	2.691		
2Tb			
Selected bond distances, Å			
Tb1-N1	2.5503(18)	Tb2-N13	2.631(2)
Tb1-N11	2.5653(19)	Tb2-N15	2.535(2)
Tb1-N3	2.5475(18)	Tb2-N17	2.493(2)
Tb1-N5	2.4947(19)	Tb2-N19	2.4491(19)
Tb1-N7	2.5659(19)	Tb2-N21	2.563(2)
Tb1-N9	2.4663(18)	Tb2-N23	2.4953(19)
Tb1-O1	2.2761(15)	Tb2-O3	2.2879(15)
Tb1-O2	2.2761(16)	Tb2-O4	2.2733(15)
Selected angles, º			
O2-Tb1-O1	73.01(6)	O4-Tb2-O3	72.27(5)
O2-Tb1-N9	136.01(6)	O4-Tb2-N19	142.42(6)
O1-Tb1-N9	75.35(6)	O3-Tb2-N19	82.52(6)
O2-Tb1-N5	76.13(6)	O4-Tb2-N17	73.26(6)
O1-Tb1-N5	136.53(6)	O3-Tb2-N17	126.19(6)
N9-Tb1-N5	145.53(6)	N19-Tb2-N17	143.73(7)
O2-Tb1-N3	147.72(6)	O4-Tb2-N23	105.26(6)
O1-Tb1-N3	117.94(6)	O3-Tb2-N23	146.48(6)
N9-Tb1-N3	75.14(6)	N19-Tb2-N23	80.86(7)
N5-Tb1-N3	76.66(6)	N17-Tb2-N23	82.30(7)
O2-Tb1-N1	84.54(6)	O4-Tb2-N15	101.36(6)
O1-Tb1-N1	74.06(6)	O3-Tb2-N15	73.94(6)
N9-Tb1-N1	114.97(6)	N19-Tb2-N15	97.74(7)
N5-Tb1-N1	73.20(6)	N17-Tb2-N15	73.90(7)
N3-Tb1-N1	71.19(6)	N23-Tb2-N15	137.11(6)
O2-Tb1-N11	74.85(6)	O4-Tb2-N21	76.00(6)
O1-Tb1-N11	83.91(6)	O3-Tb2-N21	77.58(6)
N9-Tb1-N11	72.10(6)	N19-Tb2-N21	71.59(6)
N5-Tb1-N11	116.48(6)	N17-Tb2-N21	130.55(7)
N3-Tb1-N11	133.82(6)	N23-Tb2-N21	69.62(6)
N1-Tb1-N11	153.46(6)	N15-Tb2-N21	150.70(6)
O2-Tb1-N7	117.90(6)	O4-Tb2-N13	146.76(6)
O1-Tb1-N7	147.11(6)	O3-Tb2-N13	130.80(6)
N9-Tb1-N7	77.01(6)	N19-Tb2-N13	70.51(7)

N5-Tb1-N7	75.28(6)	N17-Tb2-N13	73.52(7)
N3-Tb1-N7	70.75(6)	N23-Tb2-N13	69.16(6)
N1-Tb1-N7	134.91(6)	N15-Tb2-N13	70.09(6)
N11-Tb1-N7	70.84(6)	N21-Tb2-N13	127.14(6)
Weak intermolecular contacts, Å			
H6-C21	2.792	H9-H58B	2.393
H3-C20	2.715	H15-H57B	2.199
H3-C21	2.850	H41B-H66B	2.132
C7-H29	2.750	C30-H62	2.829
H29-N5	2.728	C33-H64A	2.717
C8-C8	3.394	H33-H64A	2.329
H14-N2	2.701	C27-H63A	2.831
C13-H35	2.735	H27-H63A	2.355
C18-H36	2.650	H54B-C64	2.879
H25-C32	2.894	H54B-H64B	2.095
2Dy			
Selected bond distances, Å			
Dy1-N10	2.558(5)	Dy2-N14	2.606(5)
Dy1-N12	2.538(5)	Dy2-N16	2.487(5)
Dy1-N2	2.474(5)	Dy2-N18	2.527(5)
Dy1-N4	2.531(5)	Dy2-N20	2.480(5)
Dy1-N6	2.522(5)	Dy2-N22	2.439(5)
Dy1-N8	2.449(5)	Dy2-N24	2.519(5)
Dy1-O1	2.257(3)	Dy2-O3	2.260(4)
Dy1-O2	2.270(4)	Dy2-O4	2.287(4)
Selected angles, º			
O1-Dy1-O2	72.38(13)	O3-Dy2-O4	71.74(14)
O1-Dy1-N8	73.86(14)	O3-Dy2-N22	145.00(14)
O2-Dy1-N8	135.19(14)	O4-Dy2-N22	84.81(14)
O1-Dy1-N2	135.65(15)	O3-Dy2-N20	105.87(15)
O2-Dy1-N2	75.48(14)	O4-Dy2-N20	145.92(15)
N8-Dy1-N2	147.74(15)	N22-Dy2-N20	79.30(16)
O1-Dy1-N6	74.30(14)	O3-Dy2-N16	71.49(15)
O2-Dy1-N6	86.41(14)	O4-Dy2-N16	125.37(15)
N8-Dy1-N6	111.65(15)	N22-Dy2-N16	142.83(16)
N2-Dy1-N6	73.97(16)	N20-Dy2-N16	82.97(16)
O1-Dy1-N4	117.95(14)	O3-Dy2-N24	76.14(14)
O2-Dy1-N4	149.16(15)	O4-Dy2-N24	76.34(14)
N8-Dy1-N4	74.11(15)	N22-Dy2-N24	73.25(16)
N2-Dy1-N4	78.61(15)	N20-Dy2-N24	70.29(15)
N6-Dy1-N4	70.46(15)	N16-Dy2-N24	129.89(17)
O1-Dy1-N12	84.79(14)	O3-Dy2-N18	99.95(15)
O2-Dy1-N12	76.65(15)	O4-Dy2-N18	72.76(14)
N8-Dy1-N12	71.73(15)	N22-Dy2-N18	97.30(16)
N2-Dy1-N12	116.43(15)	N20-Dy2-N18	138.84(16)
N6-Dy1-N12	156.34(15)	N16-Dy2-N18	75.47(16)
N4-Dy1-N12	130.84(16)	N24-Dy2-N18	148.40(16)
O1-Dy1-N10	148.74(15)	O3-Dy2-N14	143.37(15)
O2-Dy1-N10	117.62(13)	O4-Dy2-N14	132.32(15)
N8-Dy1-N10	80.35(15)	N22-Dy2-N14	71.40(15)
N2-Dy1-N10	74.30(16)	N20-Dy2-N14	69.91(15)
N6-Dy1-N10	132.96(15)	N16-Dy2-N14	71.89(16)

N4-Dy1-N10	69.92(15)	N24-Dy2-N14	130.43(15)
N12-Dy1-N10	70.38(15)	N18-Dy2-N14	70.21(15)
Weak intermolecular contacts, Å			
H4-C19	2.750	H32-N2	2.730
C18-H34	2.729	C25-H49	2.889
N12-H34	2.682	H41A-H50A	2.371
C7-H11	2.895	B3-H49	3.095
H11-N5	2.741	C21-H53	2.855
C13-H23	2.885	C28-H52	2.808
C17-H28	2.708	H28-H52	2.337
H7-C19	2.829	C10-C48	3.360
H7-C20	2.608	H10-C48	2.766
H7-C21	2.851		
3Eu			
Selected bond distances, Å			
Eu1-O1	2.308(3)	Eu1-N9	2.545(4)
Eu1-N1	2.520(4)	Eu1-N5	2.547(4)
Eu1-O2	2.342(3)	Eu1-N3	2.559(4)
Eu1-N11	2.540(4)	Eu1-N7	2.606(4)
Selected angles, º			
O1-Eu1-O2	71.13(10)	N9-Eu1-N5	145.12(11)
O1-Eu1-N1	104.40(11)	O1-Eu1-N3	74.82(11)
O2-Eu1-N1	146.23(12)	O2-Eu1-N3	76.00(11)
O1-Eu1-N11	94.98(11)	N1-Eu1-N3	70.66(12)
O2-Eu1-N11	75.12(11)	N11-Eu1-N3	151.11(11)
N1-Eu1-N11	138.14(12)	N9-Eu1-N3	127.22(11)
O1-Eu1-N9	72.86(11)	N5-Eu1-N3	69.22(11)
O2-Eu1-N9	128.26(11)	O1-Eu1-N7	147.61(11)
N1-Eu1-N9	78.42(12)	O2-Eu1-N7	129.12(11)
N11-Eu1-N9	72.36(11)	N1-Eu1-N7	72.59(12)
O1-Eu1-N5	139.79(11)	N11-Eu1-N7	71.35(12)
O2-Eu1-N5	83.08(11)	N9-Eu1-N7	75.00(11)
N1-Eu1-N5	80.32(12)	N5-Eu1-N7	72.40(11)
N11-Eu1-N5	107.84(11)	N3-Eu1-N7	130.14(12)
Weak intermolecular contacts, Å			
C6-C6	3.301	N10-H17	2.710
H7-H13	2.344	O2-H27B	2.598
C16-H19B	2.845	C4-H27B	2.824
H11-H3	2.341	C4-Cl1	3.379
C19-H18	2.847	H4-Cl1	2.871
C20-H18	2.855	H1-Cl2	2.934
3Gd			
Selected bond distances, Å			
Gd1-O1	2.2944(9)	Gd1-N1	2.5309(11)
Gd1-O2	2.3045(9)	Gd1-N6	2.5407(10)
Gd1-N4	2.4764(10)	Gd1-N9	2.5490(11)
Gd1-N12	2.5265(11)	Gd1-N7	2.5878(10)
Selected angles, º			
O1-Gd1-O2	72.69(3)	N1-Gd1-N6	69.68(3)
O1-Gd1-N4	140.42(3)	O1-Gd1-N9	91.42(4)
O2-Gd1-N4	75.74(3)	O2-Gd1-N9	73.44(4)

O1-Gd1-N12	73.67(4)	N4-Gd1-N9	101.91(4)
O2-Gd1-N12	132.47(4)	N12-Gd1-N9	74.85(4)
N4-Gd1-N12	145.72(4)	N1-Gd1-N9	150.89(4)
O1-Gd1-N1	77.10(3)	N6-Gd1-N9	138.61(4)
O2-Gd1-N1	77.60(3)	O1-Gd1-N7	145.31(3)
N4-Gd1-N1	73.29(3)	O2-Gd1-N7	125.03(3)
N12-Gd1-N1	125.32(4)	N4-Gd1-N7	73.62(3)
O1-Gd1-N6	114.64(3)	N12-Gd1-N7	73.35(4)
O2-Gd1-N6	143.00(3)	N1-Gd1-N7	132.28(3)
N4-Gd1-N6	78.67(3)	N6-Gd1-N7	70.87(3)
N12-Gd1-N6	82.13(4)	N9-Gd1-N7	69.79(4)
Weak intermolecular contacts, Å			
H1B-H9	2.374	N8-H13	2.716
C11-C5	3.375	H10-C27	2.873
H16-N2	2.636	H23-C27	2.666
H16-C11	2.690	H23-C32	2.623
H16-B1	3.158		
3Tb			
Selected bond distances, Å			
Tb1-O2	2.2767(18)	Tb1-N10	2.523(2)
Tb1-O1	2.2894(17)	Tb1-N6	2.525(2)
Tb1-N12	2.462(2)	Tb1-N8	2.539(2)
Tb1-N2	2.516(2)	Tb1-N4	2.570(2)
Selected angles, º			
O2-Tb1-O1	72.89(6)	N10-Tb1-N6	69.94(7)
O2-Tb1-N12	140.63(7)	O2-Tb1-N8	90.93(7)
O1-Tb1-N12	75.63(6)	O1-Tb1-N8	73.46(7)
O2-Tb1-N2	73.49(7)	N12-Tb1-N8	102.21(7)
O1-Tb1-N2	132.83(7)	N2-Tb1-N8	75.01(8)
N12-Tb1-N2	145.67(7)	N10-Tb1-N8	150.83(7)
O2-Tb1-N10	77.12(7)	N6-Tb1-N8	138.55(7)
O1-Tb1-N10	77.59(7)	O2-Tb1-N4	145.19(7)
N12-Tb1-N10	73.50(7)	O1-Tb1-N4	124.93(7)
N2-Tb1-N10	124.87(8)	N12-Tb1-N4	73.51(7)
O2-Tb1-N6	114.64(7)	N2-Tb1-N4	73.51(7)
O1-Tb1-N6	143.19(7)	N10-Tb1-N4	132.36(7)
N12-Tb1-N6	78.88(7)	N6-Tb1-N4	70.72(7)
N2-Tb1-N6	81.55(7)	N8-Tb1-N4	70.07(7)
Weak intermolecular contacts, Å			
B2-H16	3.170	H18-C44	2.892
N9-H16	2.643	N8-H56A	2.720
C18-H16	2.695	C27-H56A	2.711
C33-C18	3.387	C28-H56A	2.835
N3-H22	2.715	C29-H56A	2.870
H29-C43	2.635	H37B-H56C	2.379
H29-C44	2.667		
3Dy			
Selected bond distances, Å			
Dy1-N2	2.5095(15)	Dy1-N10	2.5289(16)
Dy1-N4	2.5124(14)	Dy1-N12	2.5004(16)
Dy1-N6	2.4456(15)	Dy1-O3	2.2597(13)
Dy1-N8	2.5555(14)	Dy1-O4	2.2793(12)

Selected angles, º			
O3-Dy1-O4	73.28(5)	N2-Dy1-N4	70.09(5)
O3-Dy1-N6	140.68(5)	O3-Dy1-N10	91.08(5)
O4-Dy1-N6	75.13(4)	O4-Dy1-N10	73.41(5)
O3-Dy1-N12	73.23(5)	N6-Dy1-N10	101.75(5)
O4-Dy1-N12	133.22(5)	N12-Dy1-N10	75.54(5)
N6-Dy1-N12	145.88(5)	N2-Dy1-N10	150.63(5)
O3-Dy1-N2	76.95(5)	N4-Dy1-N10	138.61(5)
O4-Dy1-N2	77.45(5)	O3-Dy1-N8	145.25(5)
N6-Dy1-N2	73.83(5)	O4-Dy1-N8	124.83(5)
N12-Dy1-N2	124.44(5)	N6-Dy1-N8	73.39(5)
O3-Dy1-N4	114.44(5)	N12-Dy1-N8	73.81(5)
O4-Dy1-N4	143.08(5)	N2-Dy1-N8	132.36(5)
N6-Dy1-N4	79.30(5)	N4-Dy1-N8	70.61(5)
N12-Dy1-N4	81.24(5)	N10-Dy1-N8	70.23(5)
Weak intermolecular contacts, Å			
C1-C23	3.384	H8-N9	2.741
H5-C1	2.684	H13-C27	2.626
H5-B1	3.149	H13-C32	2.661
H5-N1	2.622	H2-C32	2.865
H8-N7	2.700		
4Eu			
Selected bond distances, Å			
Eu1-O4	2.294(3)	Eu4-O2	2.300(3)
Eu1-O3	2.305(3)	Eu4-O1	2.324(3)
Eu1-N24	2.518(4)	Eu4-N10	2.521(4)
Eu1-N18	2.532(4)	Eu4-N8	2.534(4)
Eu1-N22	2.538(4)	Eu4-N6	2.541(4)
Eu1-N14	2.562(4)	Eu4-N2	2.555(4)
Eu1-N20	2.578(4)	Eu4-N4	2.584(4)
Eu1-N16	2.578(4)	Eu4-N12	2.585(4)
Selected angles, º			
O4-Eu1-O3	72.34(11)	O2-Eu4-O1	72.38(11)
O4-Eu1-N24	138.35(12)	O2-Eu4-N10	139.78(12)
O3-Eu1-N24	76.14(12)	O1-Eu4-N10	79.90(12)
O4-Eu1-N18	73.77(12)	O2-Eu4-N8	108.41(12)
O3-Eu1-N18	134.55(13)	O1-Eu4-N8	147.24(12)
N24-Eu1-N18	146.45(13)	N10-Eu4-N8	80.32(13)
O4-Eu1-N22	114.57(13)	O2-Eu4-N6	72.52(12)
O3-Eu1-N22	144.40(13)	O1-Eu4-N6	130.84(12)
N24-Eu1-N22	78.04(13)	N10-Eu4-N6	145.86(12)
N18-Eu1-N22	78.08(13)	N8-Eu4-N6	77.14(12)
O4-Eu1-N14	85.44(12)	O2-Eu4-N2	91.08(12)
O3-Eu1-N14	74.66(12)	O1-Eu4-N2	76.10(12)
N24-Eu1-N14	111.69(12)	N10-Eu4-N2	110.11(12)
N18-Eu1-N14	73.29(13)	N8-Eu4-N2	135.63(12)
N22-Eu1-N14	138.55(13)	N6-Eu4-N2	71.29(12)
O4-Eu1-N20	75.05(12)	O2-Eu4-N4	148.39(12)
O3-Eu1-N20	79.16(13)	O1-Eu4-N4	124.96(12)
N24-Eu1-N20	72.84(12)	N10-Eu4-N4	71.81(12)
N18-Eu1-N20	119.60(13)	N8-Eu4-N4	71.99(13)

N22-Eu1-N20	70.03(13)	N6-Eu4-N4	76.99(12)
N14-Eu1-N20	151.11(13)	N2-Eu4-N4	71.13(12)
O4-Eu1-N16	146.59(12)	O2-Eu4-N12	75.60(13)
O3-Eu1-N16	121.29(12)	O1-Eu4-N12	78.16(12)
N24-Eu1-N16	74.12(12)	N10-Eu4-N12	70.54(13)
N18-Eu1-N16	76.70(13)	N8-Eu4-N12	70.73(13)
N22-Eu1-N16	73.42(13)	N6-Eu4-N12	123.79(12)
N14-Eu1-N16	71.29(12)	N2-Eu4-N12	153.61(12)
N20-Eu1-N16	134.65(12)	N4-Eu4-N12	130.30(13)
Weak intermolecular contacts, Å			
H35-N19	2.727	H34-C4	2.876
H13-C22	2.868	H34-C5	2.728
H13-C23	2.841	H34-H5	2.316
C7-H19	2.691	C34-H56	2.600
H44-H48C	2.296	C15-C59	3.393
H1-C25	2.733	H25-H54	2.132
H37C-H44	2.323		
4Gd			
Selected bond distances, Å			
Gd1-O2	2.3031(19)	Gd2-O3	2.312(2)
Gd1-O1	2.306(2)	Gd2-O4	2.321(2)
Gd1-N1	2.506(2)	Gd2-N19	2.491(3)
Gd1-N11	2.512(3)	Gd2-N15	2.507(2)
Gd1-N9	2.550(2)	Gd2-N22	2.537(3)
Gd1-N5	2.564(2)	Gd2-N24	2.556(2)
Gd1-N7	2.569(2)	Gd2-N13	2.556(3)
Gd1-N3	2.571(2)	Gd2-N17	2.583(3)
Selected angles, º			
O2-Gd1-O1	73.08(7)	O3-Gd2-O4	72.53(7)
O2-Gd1-N1	138.35(8)	O3-Gd2-N19	77.19(9)
O1-Gd1-N1	78.20(8)	O4-Gd2-N19	139.72(8)
O2-Gd1-N11	74.18(8)	O3-Gd2-N15	134.68(9)
O1-Gd1-N11	134.49(7)	O4-Gd2-N15	74.35(8)
N1-Gd1-N11	144.81(8)	N19-Gd2-N15	144.64(9)
O2-Gd1-N9	85.72(8)	O3-Gd2-N22	145.52(8)
O1-Gd1-N9	74.30(8)	O4-Gd2-N22	115.06(8)
N1-Gd1-N9	114.80(8)	N19-Gd2-N22	77.66(9)
N11-Gd1-N9	72.56(8)	N15-Gd2-N22	77.40(8)
O2-Gd1-N5	112.22(8)	O3-Gd2-N24	78.79(8)
O1-Gd1-N5	146.19(8)	O4-Gd2-N24	76.07(8)
N1-Gd1-N5	77.43(8)	N19-Gd2-N24	72.47(9)
N11-Gd1-N5	76.31(8)	N15-Gd2-N24	121.52(9)
N9-Gd1-N5	137.91(8)	N22-Gd2-N24	71.38(8)
O2-Gd1-N7	146.73(7)	O3-Gd2-N13	74.16(9)
O1-Gd1-N7	121.55(8)	O4-Gd2-N13	86.79(8)
N1-Gd1-N7	74.62(8)	N19-Gd2-N13	109.87(10)
N11-Gd1-N7	75.67(8)	N15-Gd2-N13	73.95(9)
N9-Gd1-N7	72.05(8)	N22-Gd2-N13	137.28(8)
N5-Gd1-N7	73.32(8)	N24-Gd2-N13	151.32(9)
O2-Gd1-N3	75.45(7)	O3-Gd2-N17	122.17(8)
O1-Gd1-N3	78.29(8)	O4-Gd2-N17	145.48(8)
N1-Gd1-N3	69.61(8)	N19-Gd2-N17	74.04(9)

N11-Gd1-N3	122.11(8)	N15-Gd2-N17	74.65(9)
N9-Gd1-N3	150.29(8)	N22-Gd2-N17	71.96(8)
N5-Gd1-N3	71.44(8)	N24-Gd2-N17	134.42(8)
N7-Gd1-N3	133.98(7)	N13-Gd2-N17	70.33(9)
Weak intermolecular contacts, Å			
H38-C2	2.827	C4-H19B	2.795
H38-H2	2.302	C2-H50	2.692
C47-C6	3.398	C10-H14	2.857
C33-H37	2.715	H21A-H59B	2.284
C47-H51	2.811	C37-H58A	2.832
C48-H51	2.849		
4Tb			
Selected bond distances, Å			
Tb1-N10	2.561(4)	Tb2-N14	2.557(5)
Tb1-N12	2.470(4)	Tb2-N16	2.551(4)
Tb1-N2	2.552(4)	Tb2-N18	2.485(4)
Tb1-N4	2.490(4)	Tb2-N20	2.487(4)
Tb1-N6	2.559(4)	Tb2-N22	2.530(5)
Tb1-N8	2.540(4)	Tb2-N24	2.524(4)
Tb1-O1	2.284(4)	Tb2-O3	2.307(3)
Tb1-O2	2.298(3)	Tb2-O4	2.289(4)
Selected angles, º			
O1-Tb1-O2	73.17(12)	O4-Tb2-O3	72.84(13)
O1-Tb1-N12	134.00(13)	O4-Tb2-N18	74.35(14)
O2-Tb1-N12	72.96(14)	O3-Tb2-N18	136.23(14)
O1-Tb1-N4	79.82(13)	O4-Tb2-N20	139.49(14)
O2-Tb1-N4	139.31(14)	O3-Tb2-N20	76.31(14)
N12-Tb1-N4	144.26(15)	N18-Tb2-N20	144.62(15)
O1-Tb1-N8	74.81(13)	O4-Tb2-N24	116.96(13)
O2-Tb1-N8	86.21(13)	O3-Tb2-N24	144.90(14)
N12-Tb1-N8	72.77(14)	N18-Tb2-N24	76.81(15)
N4-Tb1-N8	115.53(13)	N20-Tb2-N24	76.71(15)
O1-Tb1-N2	78.22(13)	O4-Tb2-N22	75.66(14)
O2-Tb1-N2	74.70(13)	O3-Tb2-N22	79.53(14)
N12-Tb1-N2	120.66(14)	N18-Tb2-N22	118.90(15)
N4-Tb1-N2	70.35(14)	N20-Tb2-N22	73.43(15)
N8-Tb1-N2	150.52(14)	N24-Tb2-N22	71.55(14)
O1-Tb1-N6	147.07(13)	O4-Tb2-N16	143.87(16)
O2-Tb1-N6	111.65(13)	O3-Tb2-N16	121.74(14)
N12-Tb1-N6	75.47(14)	N18-Tb2-N16	74.08(16)
N4-Tb1-N6	76.79(14)	N20-Tb2-N16	75.62(16)
N8-Tb1-N6	136.68(14)	N24-Tb2-N16	71.75(15)
N2-Tb1-N6	72.28(14)	N22-Tb2-N16	136.22(16)
O1-Tb1-N10	122.22(13)	O4-Tb2-N14	84.34(15)
O2-Tb1-N10	146.59(13)	O3-Tb2-N14	74.17(14)
N12-Tb1-N10	76.52(14)	N18-Tb2-N14	74.52(15)
N4-Tb1-N10	73.98(14)	N20-Tb2-N14	111.74(16)
N8-Tb1-N10	71.92(13)	N24-Tb2-N14	137.53(14)
N2-Tb1-N10	134.36(13)	N22-Tb2-N14	150.70(15)
N6-Tb1-N10	72.60(14)	N16-Tb2-N14	70.67(16)
Weak intermolecular contacts, Å			
C52-C19	3.389	C39-C40	3.334

H16C-H21	2.386	C21-H49	2.675
H41-C20	2.851	H21-H49	2.389
H41-H20	2.360	H27-C29	2.883
H41-C21	2.817	H5A-C17	2.893
H41-H21	2.348	H37-C59	2.736
H34-C40	2.824	H37-H59C	2.329
H48-C51	2.820	H43-C53	2.806
H48-C52	2.801	H43-C58	2.866
C37-H39	2.793	H25-H59A	2.336
C38-C40	3.332	H45-H54	2.279
4Dy			
Selected bond distances, Å			
Dy1-O2	2.266(2)	Dy2-O3	2.258(2)
Dy1-O1	2.2730(19)	Dy2-O4	2.2828(19)
Dy1-N12	2.469(3)	Dy2-N24	2.483(2)
Dy1-N6	2.494(2)	Dy2-N22	2.489(2)
Dy1-N8	2.510(2)	Dy2-N16	2.511(2)
Dy1-N2	2.519(2)	Dy2-N18	2.513(2)
Dy1-N10	2.548(2)	Dy2-N14	2.550(2)
Dy1-N4	2.549(2)	Dy2-N20	2.561(3)
Selected angles, º			
O2-Dy1-O1	73.52(7)	O3-Dy2-O4	73.36(7)
O2-Dy1-N12	138.75(8)	O3-Dy2-N24	140.07(7)
O1-Dy1-N12	75.05(8)	O4-Dy2-N24	78.83(8)
O2-Dy1-N6	73.02(7)	O3-Dy2-N22	108.37(8)
O1-Dy1-N6	134.96(7)	O4-Dy2-N22	147.19(7)
N12-Dy1-N6	146.94(8)	N24-Dy2-N22	80.87(8)
O2-Dy1-N8	114.37(8)	O3-Dy2-N16	71.79(7)
O1-Dy1-N8	144.59(7)	O4-Dy2-N16	131.23(7)
N12-Dy1-N8	78.86(8)	N24-Dy2-N16	146.46(8)
N6-Dy1-N8	77.75(8)	N22-Dy2-N16	77.09(8)
O2-Dy1-N2	85.70(8)	O3-Dy2-N18	90.99(8)
O1-Dy1-N2	74.46(7)	O4-Dy2-N18	75.66(7)
N12-Dy1-N2	110.70(8)	N24-Dy2-N18	109.34(8)
N6-Dy1-N2	73.80(8)	N22-Dy2-N18	135.91(7)
N8-Dy1-N2	138.23(8)	N16-Dy2-N18	71.96(8)
O2-Dy1-N10	75.07(8)	O3-Dy2-N14	148.30(7)
O1-Dy1-N10	79.05(7)	O4-Dy2-N14	124.37(8)
N12-Dy1-N10	73.30(8)	N24-Dy2-N14	71.60(8)
N6-Dy1-N10	119.44(8)	N22-Dy2-N14	71.75(8)
N8-Dy1-N10	70.73(8)	N16-Dy2-N14	77.61(8)
N2-Dy1-N10	150.78(8)	N18-Dy2-N14	71.52(8)
O2-Dy1-N4	146.39(7)	O3-Dy2-N20	75.36(8)
O1-Dy1-N4	120.70(8)	O4-Dy2-N20	78.06(7)
N12-Dy1-N4	73.90(8)	N24-Dy2-N20	71.24(8)
N6-Dy1-N4	77.12(8)	N22-Dy2-N20	71.10(8)
N8-Dy1-N4	73.02(8)	N16-Dy2-N20	123.23(8)
N2-Dy1-N4	71.30(8)	N18-Dy2-N20	152.96(8)
N10-Dy1-N4	134.73(8)	N14-Dy2-N20	130.51(8)
Weak intermolecular contacts, Å			
N9-H17	2.685	H37C-H45	2.253
H8-C4	2.899	C19-H16	2.840

C19-H23	2.874	C20-H16	2.720
H35-N19	2.717	H20-H16	2.326
H34-C4	2.836	H32-C53	2.893
H34-C5	2.842	H32-C54	2.725
C7-H25	2.713	H32-C55	2.852
H45-H52B	2.281	H32-C58	2.798
H1-C22	2.672	H59B-H59B	2.046
5Eu			
Selected bond distances, Å			
Eu1-O1	2.310(2)	Eu1-N4	2.550(3)
Eu1-N1	2.545(3)	Eu1-N6	2.606(3)
Selected angles, º			
N1-Eu1-N1	75.29(12)	N6-Eu1-N6	146.70(12)
N1-Eu1-N4	75.82(9)	O1-Eu1-N1	115.98(9)
N1-Eu1-N4	74.97(9)	O1-Eu1-N1	146.15(8)
N1-Eu1-N6	72.82(8)	O1-Eu1-N4	77.30(8)
N1-Eu1-N6	138.51(8)	O1-Eu1-N4	136.89(8)
N4-Eu1-N4	142.87(12)	O1-Eu1-N6	73.39(8)
N4-Eu1-N6	120.74(9)	O1-Eu1-N6	80.02(8)
N4-Eu1-N6	70.81(8)	O1-Eu1-O1	73.54(11)
Weak intermolecular contacts, Å			
C20-H4	2.858	C10-H3	2.829
H5-C6	2.864	H10C-H3	2.379
5Gd			
Selected bond distances, Å			
Gd1-O1	2.302(2)	Gd1-N1	2.535(3)
Gd1-N3	2.535(3)	Gd1-N5	2.594(3)
Selected angles, º			
N1-Gd1-N1	143.19(13)	N5-Gd1-N5	146.81(13)
N1-Gd1-N5	120.22(9)	O1-Gd1-N1	76.78(9)
N1-Gd1-N5	71.16(9)	O1-Gd1-N1	137.07(9)
N3-Gd1-N1	75.61(9)	O1-Gd1-N3	146.24(9)
N3-Gd1-N1	75.39(9)	O1-Gd1-N3	115.70(9)
N3-Gd1-N3	75.03(13)	O1-Gd1-N5	80.32(9)
N3-Gd1-N5	138.36(9)	O1-Gd1-N5	73.30(9)
N3-Gd1-N5	72.89(9)	O1-Gd1-O1	74.22(12)
Weak intermolecular contacts, Å			
H8-C9	2.853	H11-C19	2.874
H8-H9	2.391	H11-C20	2.889
H14-C5	2.838	H14-H17	2.384
H14-H5C	2.396		
5Tb			
Selected bond distances, Å			
Tb5-O2	2.247(6)	Tb5-N1	2.518(3)
Tb5-O1	2.333(5)	Tb5-N7	2.535(4)
Tb5-N5	2.500(3)	Tb5-N3	2.588(4)
Selected angles, º			
N1-Tb5-N1	76.64(13)	O1-Tb5-N3	135.50(14)
N1-Tb5-N3	70.94(9)	O1-Tb5-N5	141.82(15)
N1-Tb5-N7	138.85(7)	O1-Tb5-N5	85.15(15)
N5-Tb5-N1	142.89(9)	O1-Tb5-N7	70.95(16)

N5-Tb5-N1	89.92(9)	O2-Tb5-N1	105.21(17)
N5-Tb5-N3	71.98(8)	O2-Tb5-N1	72.16(17)
N5-Tb5-N5	80.21(13)	O2-Tb5-N3	142.75(17)
N5-Tb5-N7	70.96(9)	O2-Tb5-N5	103.13(17)
N7-Tb5-N3	130.90(11)	O2-Tb5-N5	144.89(17)
O1-Tb5-N1	71.41(16)	O2-Tb5-N7	77.14(17)
O1-Tb5-N1	121.28(16)	O2-Tb5-O1	70.7(2)
Weak intermolecular contacts, Å			
H4-H12	2.349	C17-H17C	2.759
C5-H11	2.877	H17A-H19A	2.162
H5-H11	2.214	H17A-H17C	2.357
H6-B1	3.030	H17B-C19	2.506
H6-H1A	2.335	H17B-H19A	2.025
C17-C19	2.772	H17B-H19B	2.378
C17-H19A	2.236	H17C-C19	2.426
C17-H19B	2.490	H17C-H19A	2.179
C17-C17	3.374	H17C-H19B	1.878
C17-H17B	2.899		
5Dy			
Selected bond distances, Å			
Dy1-N1	2.534(3)	Dy2-N21	2.573(3)
Dy1-N11	2.482(3)	Dy2-N23	2.462(3)
Dy1-N3	2.513(3)	Dy2-O3	2.263(3)
Dy1-N5	2.490(3)	Dy2-O4	2.258(3)
Dy1-N7	2.566(3)	Dy3-N25	2.550(4)
Dy1-N9	2.516(3)	Dy3-N27	2.534(4)
Dy1-O1	2.266(3)	Dy3-N29	2.447(3)
Dy1-O2	2.269(3)	Dy3-N31	2.549(4)
Dy2-N13	2.540(3)	Dy3-N33	2.524(4)
Dy2-N15	2.457(3)	Dy3-N35	2.468(4)
Dy2-N17	2.540(3)	Dy3-O5	2.268(3)
Dy2-N19	2.509(3)	Dy3-O6	2.264(3)
Selected angles, º			
O1-Dy1-O2	73.82(10)	N19-Dy2-N17	72.60(10)
O1-Dy1-N11	74.78(10)	O4-Dy2-N13	85.70(10)
O2-Dy1-N11	136.15(10)	O3-Dy2-N13	74.01(10)
O1-Dy1-N5	137.53(10)	N15-Dy2-N13	74.55(10)
O2-Dy1-N5	74.39(11)	N23-Dy2-N13	111.91(10)
N11-Dy1-N5	146.21(11)	N19-Dy2-N13	139.91(10)
O1-Dy1-N3	118.80(10)	N17-Dy2-N13	72.08(10)
O2-Dy1-N3	146.27(10)	O4-Dy2-N21	73.53(10)
N11-Dy1-N3	76.68(11)	O3-Dy2-N21	77.67(10)
N5-Dy1-N3	77.18(11)	N15-Dy2-N21	119.45(11)
O1-Dy1-N9	144.94(10)	N23-Dy2-N21	73.46(11)
O2-Dy1-N9	117.70(10)	N19-Dy2-N21	71.27(11)
N11-Dy1-N9	75.71(11)	N17-Dy2-N21	136.79(10)
N5-Dy1-N9	75.92(11)	N13-Dy2-N21	148.55(10)
N3-Dy1-N9	71.41(10)	O6-Dy3-O5	74.00(11)
O1-Dy1-N1	75.36(10)	O6-Dy3-N29	136.82(11)
O2-Dy1-N1	82.84(10)	O5-Dy3-N29	75.29(10)
N11-Dy1-N1	117.41(10)	O6-Dy3-N35	73.69(11)
N5-Dy1-N1	73.40(11)	O5-Dy3-N35	137.10(10)

N3-Dy1-N1	71.88(10)	N29-Dy3-N35	146.17(11)
N9-Dy1-N1	136.22(11)	O6-Dy3-N33	145.10(11)
O1-Dy1-N7	80.48(10)	O5-Dy3-N33	117.37(12)
O2-Dy1-N7	73.59(10)	N29-Dy3-N33	76.89(11)
N11-Dy1-N7	71.67(10)	N35-Dy3-N33	77.73(12)
N5-Dy1-N7	116.07(11)	O6-Dy3-N27	118.00(12)
N3-Dy1-N7	136.62(10)	O5-Dy3-N27	146.71(10)
N9-Dy1-N7	72.57(10)	N29-Dy3-N27	76.32(11)
N1-Dy1-N7	150.08(10)	N35-Dy3-N27	74.78(11)
O4-Dy2-O3	74.05(11)	N33-Dy3-N27	71.93(12)
O4-Dy2-N15	73.10(11)	O6-Dy3-N31	82.18(12)
O3-Dy2-N15	135.62(11)	O5-Dy3-N31	74.85(11)
O4-Dy2-N23	139.26(10)	N29-Dy3-N31	117.72(12)
O3-Dy2-N23	76.15(10)	N35-Dy3-N31	73.47(12)
N15-Dy2-N23	145.64(11)	N33-Dy3-N31	70.70(11)
O4-Dy2-N19	113.84(11)	N27-Dy3-N31	134.93(11)
O3-Dy2-N19	143.30(10)	O6-Dy3-N25	73.88(12)
N15-Dy2-N19	78.28(11)	O5-Dy3-N25	83.18(12)
N23-Dy2-N19	76.65(11)	N29-Dy3-N25	72.97(12)
O4-Dy2-N17	144.52(10)	N35-Dy3-N25	113.58(13)
O3-Dy2-N17	122.95(10)	N33-Dy3-N25	137.34(11)
N15-Dy2-N17	74.47(11)	N27-Dy3-N25	72.12(12)
N23-Dy2-N17	75.84(10)	N31-Dy3-N25	151.17(11)
Weak intermolecular contacts, Å			
H48-N8	2.648	C26-H75	2.728
H48-N10	2.749	C28-H79	2.727
H42-C78	2.723	C22-H87	2.844
C24-H45	2.733	H22-H87	2.361
H24-C48	2.885	C41-H84	2.850
H24-C49	2.858	C77-H10E	2.851
H25-C54	2.822	N31-H10E	2.732
C53-H68	2.790	C43-H111	2.785
C29-H39	2.837	C62-H114	2.874
H29-H39	2.324	C68-H115	2.743
H13-C18	2.829	H94-H10F	2.214

Table S3. Parameters for coordination polyhedra and π-stacking interactions in the studied complexes

Compound	Angles between planes,°			Polyhedron[c]	Intramolecular Ln-Ln distance, Å	π-stacking fragments		
	δ [a]	φ[a]	ω[b]				1[d], Å or δ, °	d[d](C1-C2), Å
Square antiprism[a]	0, 0, 52.5, 52.5	24.5	77.4					
Bicapped trigonal prism[a]	0, 21.7, 48.2, 48.2	14.1						
Dodecahedron[a]	29.5, 29.5, 29.5, 29.5	0	90					
1Eu (Tp_2EuPhm)	3.82, 3.82, 60.97, 60.97	25.5, 31.9	78.78	AP	-	Ph-pz	24.24	4.021
1Gd (Tp_2GdPhm)	4.16, 4.16, 61.14, 61.14	25.1, 32.6	79.55	AP	-	Ph-pz	25.24	4.081
1Tb (Tp_2TbPhm)	4.33, 4.33, 61.33, 61.33	25.7, 32.4	79.79	AP	-	Ph-pz	25.10	4.056
1Dy (Tp_2DyPhm)	4.81, 4.81, 61.08, 61.08	25.0, 32.20	79.22	AP	-	Ph-pz	25.91	4.112
2Eu ((Tp_2Eu)$_2$Tae)	17.63, 22.67, 29.24, 35.74 1.42, 8.32, 60.20, 61.15	0.11, 3.21 24.6, 32.2	83.17 81.85	D AP	9.150			
2Gd ((Tp_2Gd)$_2$Tae)	0.77, 8.78, 59.82, 60.54 20.45, 21.06, 31.45, 35.55	24.3, 31.6 1.5, 1.6	80.05 83.76	AP D	9.114	-		
2Tb ((Tp_2Tb)$_2$Tae)	4.73, 6.07, 60.41, 60.75 19.00, 23.24, 30,70, 34.81	24.6, 31.5 0.3, 1.9	80.10 83.99	AP D	9.093	-		
2Dy ((Tp_2Dy)$_2$Tae)	3.85, 9.19, 61.15, 61.83 18.25, 23.50, 32.92, 38.91	26.6, 30.6 0.2, 3.2	81.41 83.58	AP D	9.114	-		
3Eu ((Tp_2Eu)$_2$pPhd)	16.99, 21.82, 28.99, 39.81	3.1, 8.5	82.65	D	13.455	-		
3Gd ((Tp_2Gd)$_2$pPhd)	7.00, 23.81, 35.83, 42.58	10.1, 10.3	82.91	D, AP, BTP (small differences)	13.381	-		
3Tb ((Tp_2Tb)$_2$pPhd)	6.36, 23.59, 36.40, 42.41	10.5, 10.6	83.01		13.358	-		
3Dy ((Tp_2Dy)$_2$pPhd)	6.11, 23.87, 36.54, 42.16	10.5, 10.7	83.44		13.323	-		
4Eu ((Tp_2Eu)$_2$mPhd)	0.80, 12.38, 41.48, 44.46 10.24, 16.31, 34.27, 39.63	15.4, 16.7 8.3, 11.5	81.84 82.58	AP D	11.681	-		
4Gd ((Tp_2Gd)$_2$mPhd)	6.36, 9.37, 41.59, 44.70 3.35, 14.29, 41.42, 44.35	17.2, 13.7 13.8, 16.4	81.08 81.83	AP AP	11.168	Pz-pz	3.554	3.643
4Tb ((Tp_2Tb)$_2$mPhd)	6.13, 9.19, 41.60, 45.44 1.09, 12.78, 57.50, 58.28	13.8, 17.5 21.7, 28.5	81.00 79.95	AP AP	11.136	Pz-pz	3.537	3.640
4Dy ((Tp_2Dy)$_2$mPhd)	0.95, 12.37, 41.58, 43.73 9.20, 16.55, 34.39, 39.02	15.8, 16.3 9.1, 11.1	82.68 83.13	AP D	11.610	-		
5Eu ((Tp_2Eu)$_3$Pht)	0.37, 0.37, 47.89, 52.92	25.0, 25.0	81.22	AP	11.580	Pz-pz	3.524	3.578
5Gd ((Tp_2Gd)$_3$Pht)	0.22, 0.22, 47.77, 53.41	25.2, 25.2	81.67	AP	11.554	Pz-pz	3.521	3.578

5Tb ($(Tp_2Tb)_3Pht$)	13.73, 28.08, 40.01, 41.62	3.4, 7.5	83.83	D	11.593	-		
5Dy ($(Tp_2Dy)_3Pht$)	5.01, 5.89, 60.20, 60.41	24.1, 30.0	78.96	AP	11.752, 11.217,	Pz-pz	3.444	3.609
	1.39, 14.01, 46.17, 42.98	16.5, 16.9	81.84	AP	11.524		3.573	3.658
	2.85, 7.93, 59.25, 59.85	24.0, 29.9	80.19	AP				

[a] determined as in ref. 13; [b] determined as in ref. 14; [c] determined using Shape 2.1[15]; [d] l or δ, d(C1-C2), θ and φ are characteristic of π-stacking interactions between fragments: l is the distance between planes of interacting fragments (if they lie in parallel planes), δ is the angle between planes of these fragments (if they lie in non-parallel planes), d(C1-C2) – distance between centroids of fragments.

Table S4. Intermolecular Ln-Ln distances in the crystal structures of compounds **1Ln-5Ln**

Compound	Intramolecular Ln-Ln distance, Å
1Eu	8.1668; 10.8994; 11.4830; 11.6541; 13.9535;14.8035
1Gd	8.1807; 10.9292; 11.4127; 11.5260; 14.0245; 15.0059
1Tb	8.1655; 10.8830; 11.3694; 11.4899; 13.9660; 14.9202
1Dy	8.1965; 10.9154; 11.3834; 11.4980; 14.0262; 15.0172
2Eu	8.0967; 8.2650; 9.1909; 9.4646; 9.8275; 10.9443; 11.0208;11.5377; 12.5286; 13.5177; 13.8027; 13.8365; 13.8850; 14.2197
2Gd	8.0921; 8.3032; 9.1452; 9.4742; 9.7263; 10.9307; 11.0561; 11.5616; 12.4490; 13.5631; 13.8348; 13.9607; 14.1197; 14.2183
2Tb	8.0730; 8.1769; 9.1622; 9.4302; 9.9197; 10.8979; 11.1306; 11.5802; 12.4803; 13.2777; 13.8138; 13.8636; 14.0217; 14.1505
2Dy	8.0498; 8.2739; 9.2696; 9.3820; 9.5305; 10.9336; 11.2282; 11.3246; 11.9119; 12.0068; 12.1179; 13.3116; 13.3869; 13.5128; 13.7033; 13.9963; 14.4305; 14.5471;15.0508
3Eu	7.9885; 9.7869; 11.1994; 11.2927; 11.5657; 11.6158; 13.4117; 13.7906; 13.8746; 14.9471
3Gd	8.7305; 9.1118; 10.1599; 10.6514; 12.1526; 13.1186; 14.2311; 14.7031; 14.8800; 15.1374
3Tb	8.7119; 9.1036; 10.1847; 10.6349; 12.1265; 13.1391; 14.2430; 14.6847; 14.8904; 15.1339
3Dy	8.6787; 9.0676; 10.1629; 10.5906; 12.0672; 13.1136; 14.2094; 14.6321; 14.8630; 15.0913
4Eu	7.8229; 10.0193; 10.1942; 10.8613; 11.0582; 12.1743; 12.5077; 12.6631; 14.0704; 14.7019; 14.7903; 14.8069; 14.8274; 14.8393; 14.9625
4Gd	7.8892; 8.8845; 9.0038; 9.1707; 9.4923; 9.6481; 9.6735; 11.1037; 12.0356; 12.5425; 12.5510; 12.8982; 14.3319
4Tb	7.8455; 9.0086; 9.1523; 9.3699; 9.5333; 9.5468; 9.7086; 11.0940; 11.4125; 11.8387; 11.8478; 12.4521; 12.7649; 13.4435
4Dy	7.8020; 9.9730; 10.1439; 10.7610; 11.0071; 12.0994; 12.4681; 12.5805; 13.9669; 14.5947; 14.7263; 14.7533; 14.7568; 14.7893; 14.8484
5Eu	8.5458; 9.7749; 10.0987
5Gd	8.5459; 9.7764; 10.1349
5Tb	9.3301; 9.4952; 10.9630; 11.7714; 13.4702; 14.7522; 14.9851
5Dy	8.6293; 8.7586; 8.9600; 9.4597; 9.6831; 10.3258; 11.2225; 11.2409; 11.4275; 11.5426; 11.8609; 12.2899; 12.5844; 12.7377; 13.5647; 13.9919; 14.0690; 14.2828; 14.4881; 14.7110

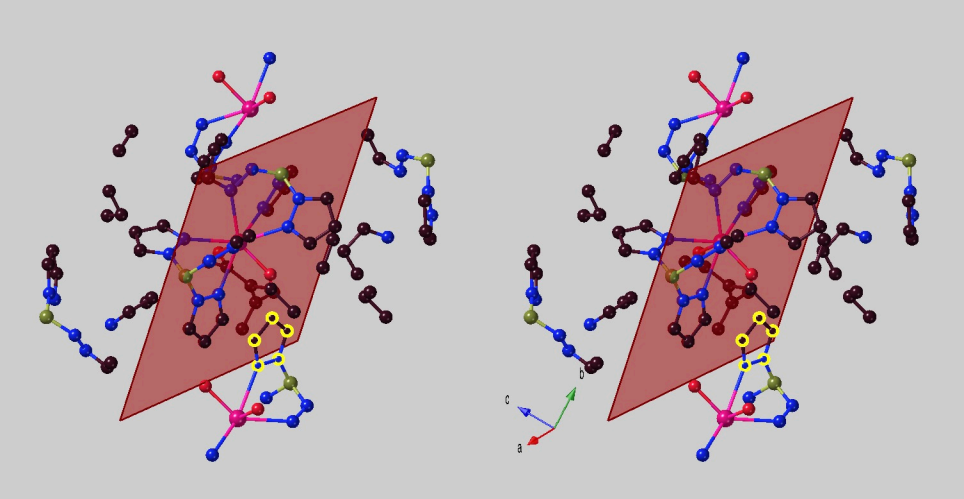


Fig. S1. Stacking interactions between two pyrazoles in **5Eu, 5Gd** and **5Tb** (b) exemplified by the Gd^{3+} compounds.

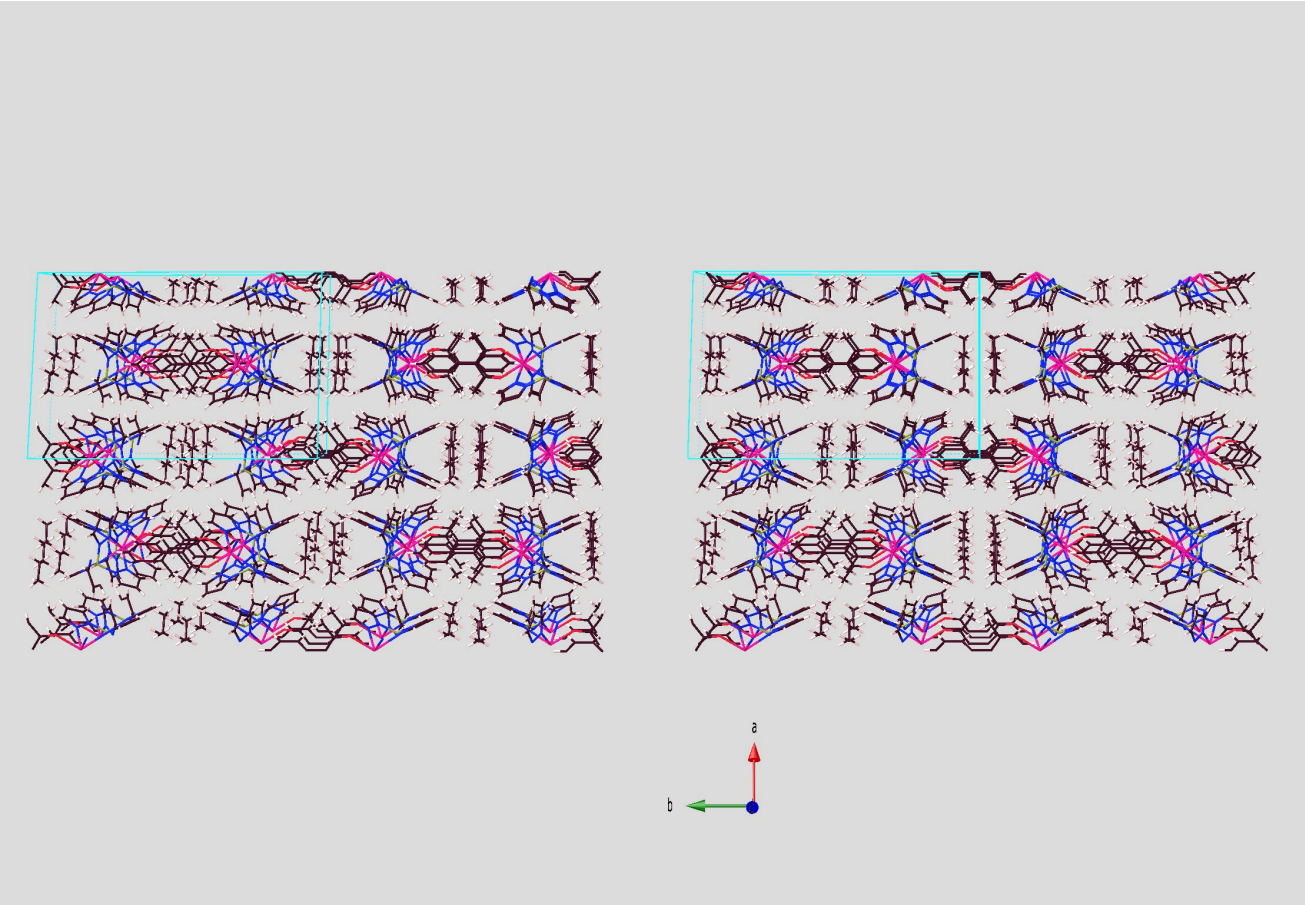


Fig. S2. Inverse stereoview of the mononuclear Eu (**1Eu**) lattice, along the *c*-direction, showing how the molecules are arranged into b/c layers along the *a*-direction. (No atoms hidden)

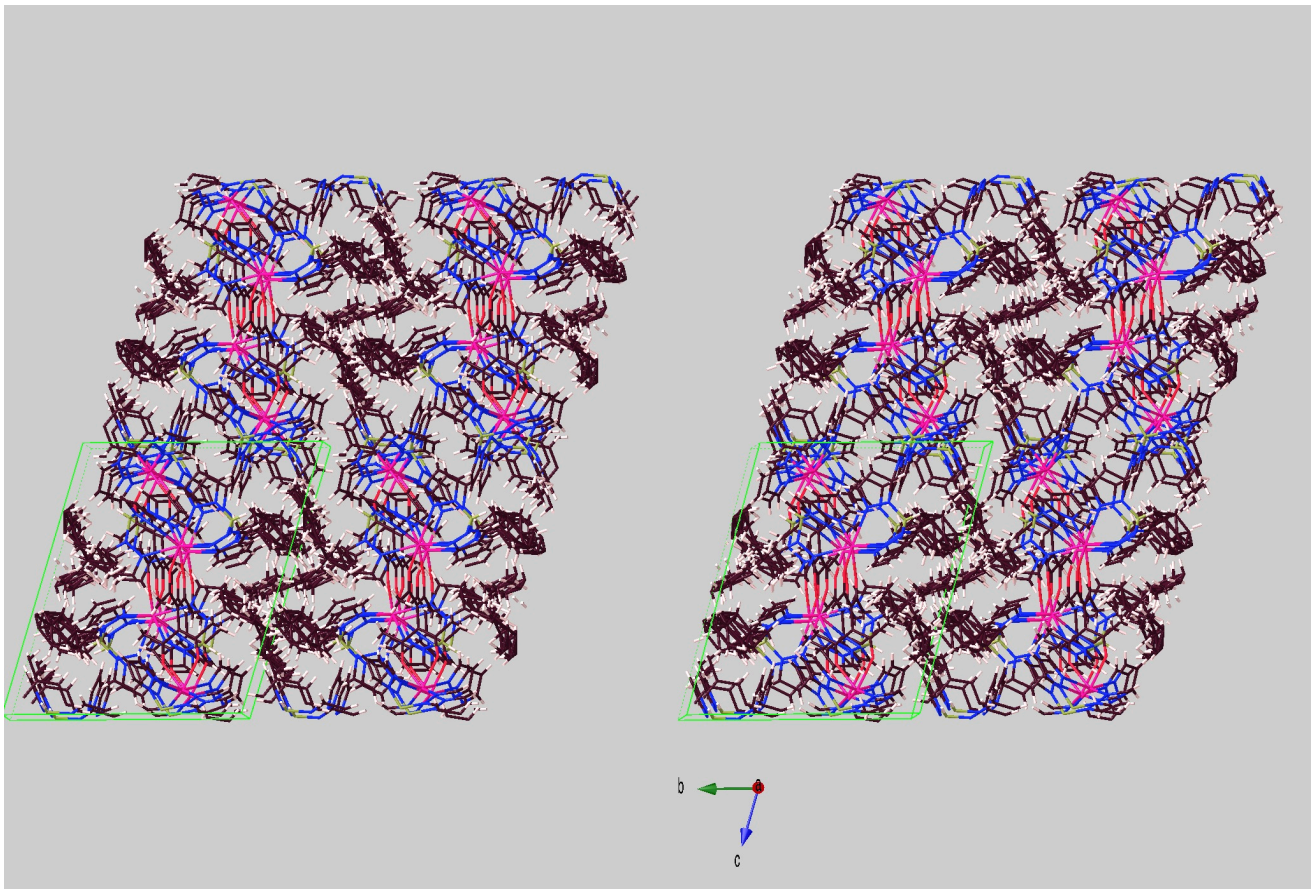


Fig. S3. Aligning of solvation voids in the Eu (**2Eu**) lattice along the *a*-direction. These voids do not form channels. Similarly along the *b*- and *c*-directions, solvation voids alternate with parts of the dinuclear molecules. (Inverse stereoview)

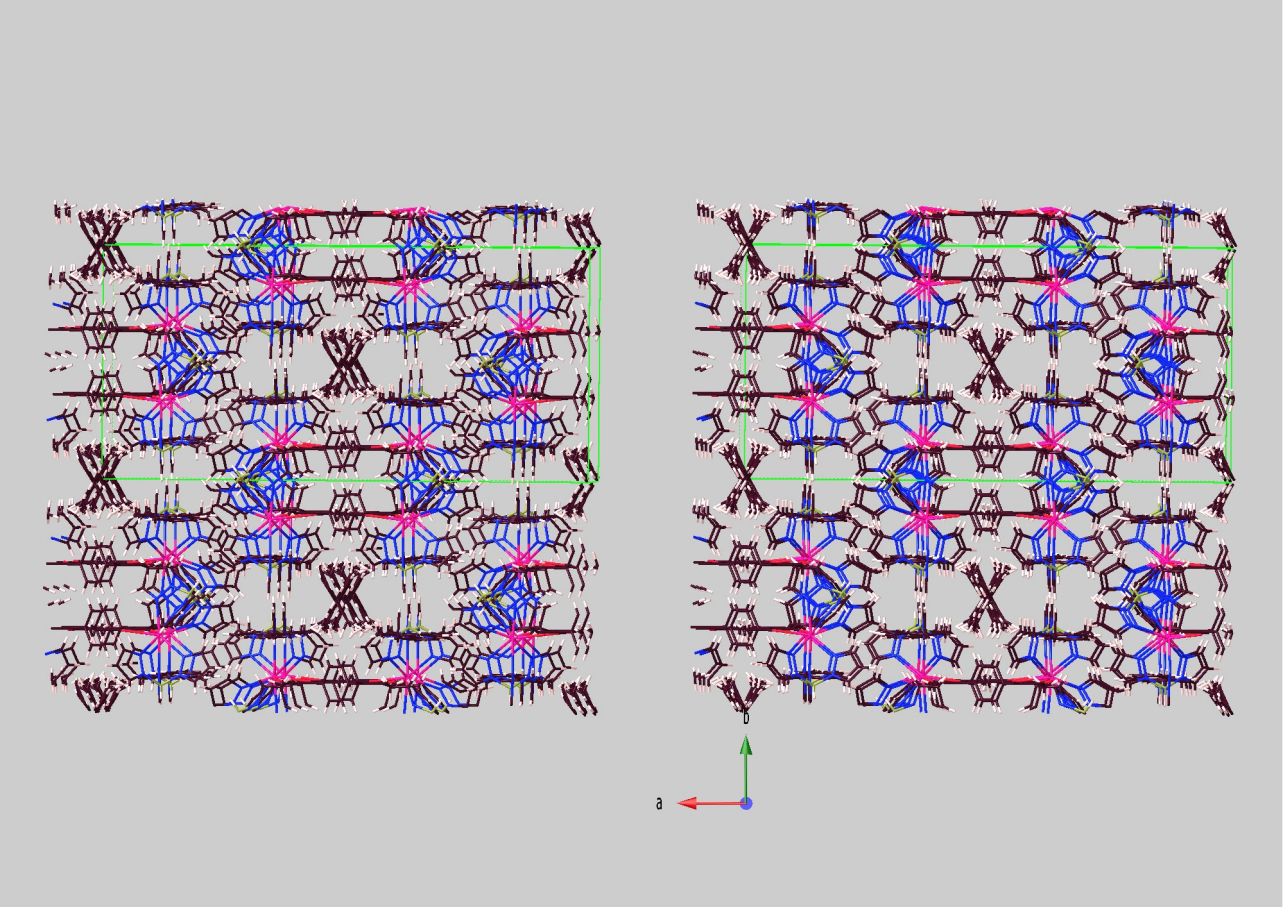


Fig. S4. Inverse stereoview along the *c*-direction of the **3Tb** lattice, showing the (disordered) hydrocarbon solvent channels. The dinuclear molecules slightly interdigitate, but generate these voids/channels. The toluenes are ordered and aligned parallel to the *ac* plane. The linking phenylenes are lined up inclined at 79.5° to the *ab* plane.

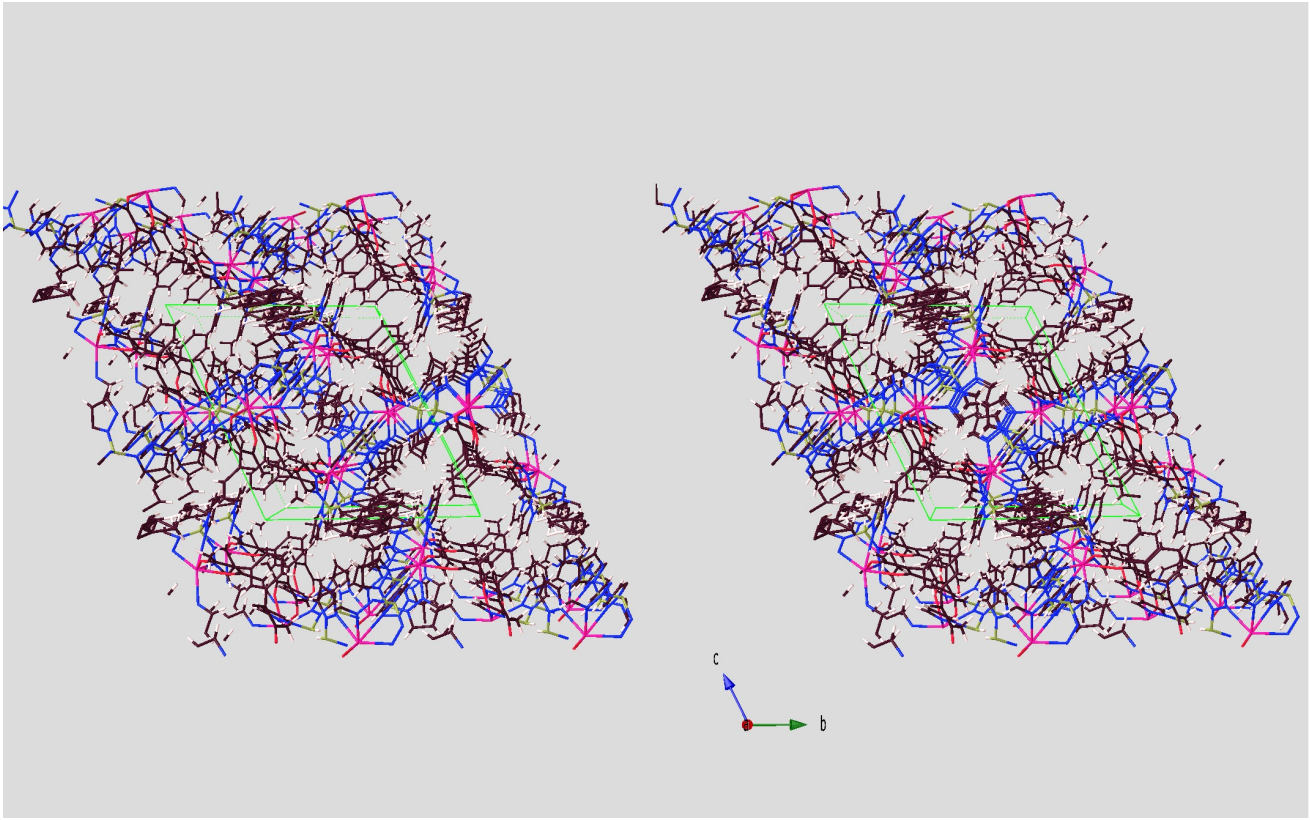


Fig. S5. An inverse stereoview along the *a*-direction (stick model) of group (0,–2) of the compound **4Tb**. This shows the arraying of the molecules along the *a*-direction, and how they are arranged into *ab* layers along *c*, with disordered hydrocarbon solvent alternating with Tb-molecules.

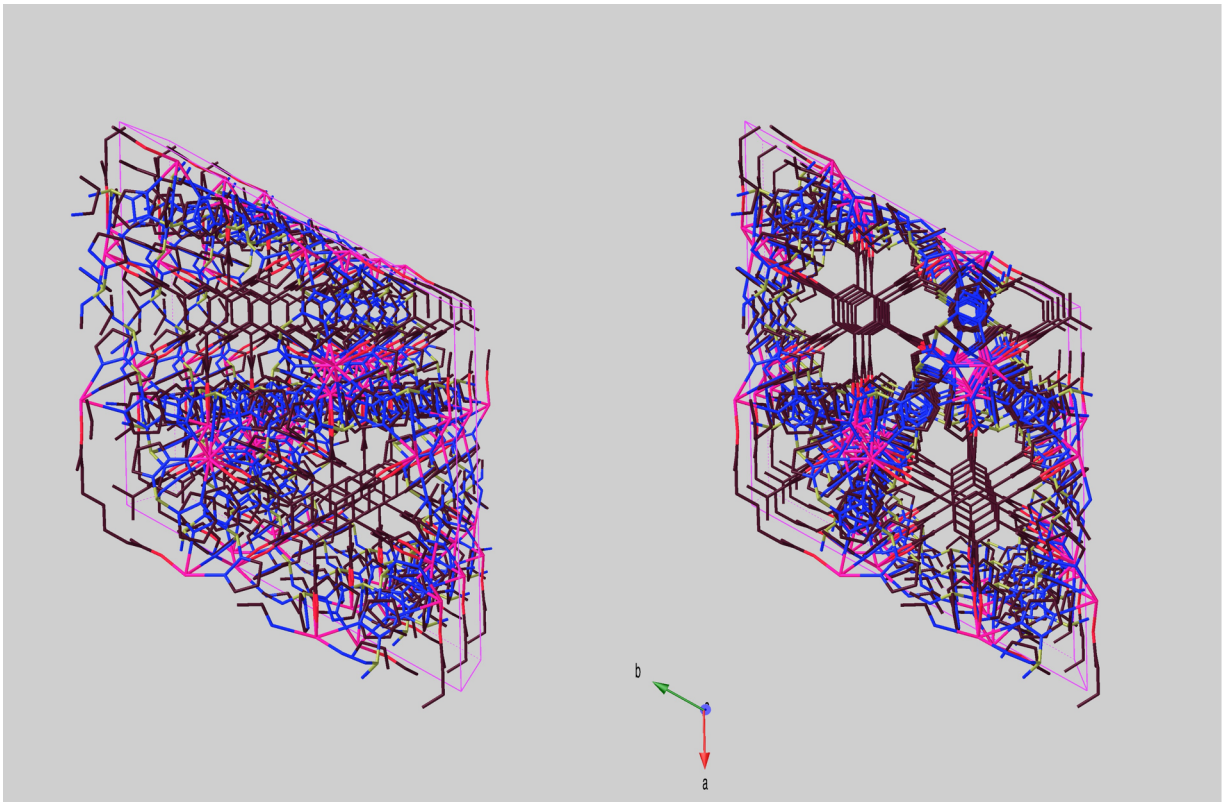


Fig. S6. Inverse stereoview of the trinuclear Gd (**5Gd**) lattice, showing arraying of the molecules along the *c*-direction. H-atoms and disordered solvating heptane deleted for clarity of viewing

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