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Ca(II), Yb(II) and Tm(III) Complexes with Tri- and Tetra-Anions of 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene

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Experimental section

Compounds **3**, **9**, **10** and **11** are sensitive to air oxygen and moisture. Therefore all manipulation on their synthesis, isolation and characterization have been conducted using Schlenk technique under vacuum or in the Glovebox (MBraun). Tetrahydrofurane and toluene were dried and stored over sodiumbenzophenone. The solvents were condensed under vacuum just prior to use into the reaction flask. THF-d_8 was dried over sodiumbenzophenone and condensed into the NMR tube that contained the sample to be analyzed. Melting points were measured in the sealed under vacuum capillaries. The Nujol mulls of the compounds were used to register their IR spectra; the spectra were recorded using FSM 1201 spectrometer. The ^{1}H NMR spectra were obtained using «Bruker DPX200» and «Bruker Avance III» spectrometers. The yields of the products were calculated on the amount of the dpp-bian used in the synthesis. Starting dpp-bian was synthesized by condensation of acenaphthenquinone with aniline in acetonitrile. 1,2-Dibromostilbene was purchased from Aldrich. In some cases elemental analyses are unsatisfactory probably due to the high sensitivity of the samples toward oxygen and moisture.

[(dpp-bian)$^{3-}$Ca^{+2}K^{+}(thf)$_2$] (2). Iodine (0.13 g, 0.5 mmol) was added to calcium shavings (10 g) in thf (30 mL). The mixture was stirred at ambient temperature till the color of iodine completely disappeared. Then the solution formed was decanted and the metal was washed with thf (2×20 mL). A solution of dpp-bian (0.5 g, 1.0 mmol) in thf (30 mL) was added to activated calcium. The reaction mixture was stirred at reflux. Within *ca*. 2 hours the mixture turned from orange to green-brown indicating the formation of [(dpp-bian)$^{2-}$Ca^{+2}(thf)$_4$] (**1**). The solution formed was added *in situ* to potassium metal 0.04 g (1.0 mmol) and the mixture was stirred at ambient temperature till potassium dissolved completely (*ca*. 8 hours). In the course of stirring the mixture turned to gold-brown. Concentration of this solution under vacuum resulted in dark crystals of complex **2** (0.14 g, 19 %). Mp. 166 °C. Found: C, 72.54; H, 7.03. $C_{44}H_{56}CaN_2KO_2$ (723). Calculated: C, 73.09; H, 7.81. ESR (20 °C, thf): g_i = 2.0028, a_H = 0.487 (1×^{1}H), a_H = 0.427 (1×^{1}H), a_H = 0.376 (1×^{1}H), a_H = 0.362 (1×^{1}H), a_H = 0.060 (1×^{1}H), a_H = 0.036 (1×^{1}H), a_N = 0.005 (2×^{14}H), a_K = 0.060 (1×^{39}K) mT. IR (Nujol): 2725 w, 2683 w,

1960 w, 1664 w, 1639 w, 1579 m, 1529 m, 1413 s, 1358 w, 1344 w, 1313 s, 1247 s, 1211 w, 1167 s, 1137 m, 1101 w, 1073 m, 1057 s, 1034 m, 880 w, 852 w, 836 w, 816 w, 786 m, 750 s, 687 m, 667 m, 623 w, 595 w, 565 w, 535 w, 524 w, 485 w, 463 s cm^{-1}.

$[(dpp\text{-}bian)^{4-}Ca^{+2}Na^{+}_{2}(thf)_4]_2$ (3). A solution of complex **1** (*in situ* as described above from 0.5 g of dpp-bian) in thf (30 mL) was added to sodium metal (0.5 g, 22 mmol). Within 8 hours at stirring the solution turned gradually to gold-brown. Complex **3** was isolated from concentrated mother liquor as red-brown crystals (0.44 g, 46 %). Mp. 152 °C. Found: C, 69.37; H, 7.83. $C_{112}H_{160}Ca_2N_4Na_4O_{10}$ (1894.55). Calculated: C, 71.00; H, 8.52. ^{1}H NMR (200 MHz, thf-d_8, 293 K, δ/ppm, *J*/Hz): 6.78 (d, 2 H, $C_6H_3Pr^i_2$, *J* = 7.2), 6.54 (d, 2 H, $C_6H_3Pr^i_2$, *J* = 7.3), 6.06 (pst, 2 H, $C_6H_3Pr^i_2$), 4.77 (pst, 2 H, naphthalene), 4.00-3.50 (m, 2 H, $CH(CH_3)_2$ + thf + 2 H, naphthalene), 3.15 (d, 2 H, naphthalene, *J* = 6.8, + s, 2 H, $CH(CH_3)_2$), 1.63 (d, 6 H, $CH(CH_3)_2$, *J* = 6.4), 1.01 (d, 6 H, $CH(CH_3)_2$, *J* = 6.4), 0.84 (d, 6 H, $CH(CH_3)_2$, *J* = 6.4), 0.75 (d, 6 H, $CH(CH_3)_2$, *J* = 6.4). IR (Nujol): 2727 w, 1672 w, 1645 w, 1612 w, 1579 s, 1562 w, 1512 m, 1496 w, 1416 w, 1402 w, 1302 m, 1186 w, 1173 w, 1153 w, 1137 w, 1101 m, 1073 m, 1046 s, 979 m, 949 w, 935 m, 916 w, 899 s, 844 m, 819 w, 786 m, 756 s, 703 s, 670 s, 642 w, 617 m, 584 w, 568 m, 551 m, 526 m, 510 m, 490 w, 466 m cm^{-1}.

$[(dpp\text{-}bian)^{4-}Ca^{+2}Li^{+}_{2}(thf)_4]_2$ (4). A solution of complex **1** (*in situ* as described above from 0.5 g of dpp-bian) in thf (30 mL) was added to lithium metal (0.5 g, 71.4 mmol). Stirring within 8 hours gave red-brown solution. The residue left after evaporation of the solvent was dissolved in toluene. Complex **4** was isolated from concentrated toluene solution as dark needle-like crystals (0.37 g, 44 %). Mp. 203 °C. Found: C, 80.03; H, 9.27. $C_{112}H_{160}Ca_2N_4Li_4O_{10}$ (1670). Calculated: C, 80.55; H, 9.66. ^{1}H NMR (200 MHz, thf-d_8, 293 K, δ/ppm, *J*/Hz): 6.84 (br s, 2 H, $C_6H_3Pr^i_2$), 6.62 (br s, 2 H, $C_6H_3Pr^i_2$), 6.25 (br s, 2 H, $C_6H_3Pr^i_2$), 4.67 (br m, 2 H, naphthalene), 3.91 (br s, 2 H, naphthalene), 3.75-3.50 (m, 2 H, $CH(CH_3)_2$ overlapping with thf signal), 3.06-2.75 (br m, 2 H, naphthalene + 2 H, $CH(CH_3)_2$), 1.90-1.70 (br m, thf), 1.66 (br s, 6 H, $CH(CH_3)_2$), 1.60 (br s, 6 H, $CH(CH_3)_2$), 1.01 (br s, 6 H, $CH(CH_3)_2$), 0.91 (br s, 6 H, $CH(CH_3)_2$). ^{13}C NMR (100.6 MHz, thf-d_8, 293 K, δ/ppm): 155.3, 142.5, 138.6, 137.5, 121.6, 121.3, 116.5, 111.1, 106.1, 97.1, 91.6, 27.1, 26.5, 25.0, 24.0, 23.6, 20.5. IR (Nujol): 1673 w, 1638 w,1603 w, 1581 m, 1565 m, 1504 w, 1469 w, 1421 m, 1405 w, 1377 m, 1349 m, 1316 m, 1239 s, 1184 m, 1156 w, 1140 m, 1109 m, 1079 m, 1032 s, 988 m, 938 m, 908 s, 883 s, 836 m, 816 w, 786 s, 756 s, 692 s, 645 w, 615 m, 582 w, 557 w, 524 s, 466 m cm^{-1}.

$[(dpp\text{-}bian)^{4-}Ca^{+2}K^{+}_{2}(thf)_4]_2$ (5). A solution of complex **1** (*in situ* as described above from 0.5 g of dpp-bian) in thf (30 mL) was added to potassium metal (0.5 g, 13 mmol). Within 8 hours at stirring the solution turned gradually to red-brown. Complex **5** was isolated from concentrated mother liquor as dark crystals (0.54 g, 62 %). Mp. 236 °C (dec). Found: C, 76.93; H, 8.87. $C_{112}H_{160}Ca_2N_4K_4O_{10}$ (1734).

Calculated: C, 77.57; H, 9.30. ^{1}H NMR (200 MHz, thf-d_8, 293 K, δ/ppm, *J*/Hz): 6.77 (d, 2 H, $C_6H_3Pr^i_2$, *J* = 7.3), 6.55 (d, 2 H, $C_6H_3Pr^i_2$, *J* = 6.3), 6.03 (pst, 2 H, $C_6H_3Pr^i_2$), 4.84 (pst, 2 H, naphthalene), 3.80-3.52 (m, 2 H, $CH(CH_3)_2$, *J* = 6.5 + m, thf), 3.46 (d, 2 H, naphthalene, *J* = 8.0), 3.21 (d, 2 H, naphthalene, *J* = 6.5), 3.12 (sept, 2 H, $CH(CH_3)_2$, *J* = 6.5), 1.95-1.66 (m, thf), 1.54 (d, 6 H, $CH(CH_3)_2$, *J* = 6.5), 1.08 (d, 6 H, $CH(CH_3)_2$, *J* = 6.5), 1.01 (d, 6 H, $CH(CH_3)_2$, *J* = 6.5), 0.75 (d, 6 H, $CH(CH_3)_2$, *J* = 6.5). ^{13}C NMR (100.6 MHz, thf-d_8, 293 K, δ/ppm): 151.4, 147.9, 136.1, 134.7, 133.3, 122.9, 123.0, 120.7, 120.6, 109.2, 104.6, 100.3, 80.0, 27.4, 26.1, 26.0, 24.4, 23.2, 22.7. IR (Nujol): 2725 w, 2680 w, 1667 m, 1639 w, 1579 m, 1562 w, 1413 m, 1399 w, 1305 m, 1247 m, 1186 w, 1170 m, 1137 w, 1104 w, 1073 w, 1057 m, 1034 m, 999 w, 976 w, 935 w, 927 m, 916 m, 899 m, 880 w, 836 m, 808 w, 786 m, 750 s, 742 w, 731 w, 689 m, 667 m, 620 w, 598 w, 579 w, 565 m, 524 w, 510 w, 488 w, 466 m cm^{-1}.

$[(dpp\text{-}bian)^{3-}Yb^{+2}K^{+}(thf)_2]$ (7). Iodine (0.25 g, 1.0 mmol) was added to ytterbium shavings (10 g) in thf (30 mL). The mixture was stirred at ambient temperature till the color of iodine completely disappeared. Then the yellowed solution of YbI_2 was decanted and the metal was washed with thf (3×20 mL). A solution of dpp-bian (0.5 g, 1.0 mmol) in thf (30 мл) was added to activated ytterbium. The reaction mixture was stirred at reflux. Within *ca*. 24 hours the mixture turned from orange to brown indicating the formation of $[(dpp\text{-}bian)^{2-}Yb^{+2}(thf)_4]$ (**6**). This solution was added *in situ* to potassium metal 0.04 g (1.0 mmol) and the mixture was stirred at ambient temperature till potassium dissolved completely (*ca*. 8 hours). In the course of stirring the mixture turned to gold-brown. The residue left after evaporation of the solvent from the reaction mixture was dissolved in benzene (40 mL). Complex **7** was isolated from concentrated benzene solution as dark crystals (0.23 g, 27 %). Mp. 263 °C. Found: C, 61.12; H, 5.97. $C_{44}H_{56}YbN_2KO_2$ (856). Calculated: C, 61.74; H, 6.59. ESR (20 °C, thf): g_i = 2.00406; a_H = 0.482 (1×^{1}H), a_H = 0.427 (1×^{1}H), a_H = 0.376 (1×^{1}H), a_H = 0.362 (1×^{1}H), a_H = 0.060 (1×^{1}H), a_H = 0.036 (1×^{1}H), a_N = 0.005 (2×^{14}N), a_K = 0.060 (1×^{39}K), a_{Yb} = 0.05 (1×^{173}Yb), a_{Yb} = 0.18 (1×^{171}Yb) mT. IR (Nujol): 2725 w, 1670 w, 1645 w, 1606 w, 1581 m, 1573 m, 1416 w, 1300 m, 1247 m, 1208 w, 1192 m, 1170 m, 1109 m, 1090 w, 1057 w, 999 w, 976 w, 935 w, 916 m, 883 w, 852 s, 816 w, 808 w, 791 m, 753 s, 678 m, 615 m, 595 w, 565 w, 540 w, 510 w, 488 w, 463 w cm^{-1}.

$[(dpp\text{-}bian)^{4-}Yb^{+2}K^{+}_2(thf)_4]_2$ (8). A solution of complex **6** (*in situ* as described above from 0.5 g of dpp-bian) in thf (30 mL) was added to potassium metal (0.5 g, 13 mmol). Within 8 hours at stirring the solution turned gold-brown. Complex **8** was isolated from concentrated mother liquor as dark crystals (0.66 g, 64 %). Mp. 92 °C (dec). Found: C, 64.13; H, 7.02. $C_{112}H_{160}Yb_2N_4K_4O_{10}$ (2078). Calculated: C, 64.73; H, 7.76. ^{1}H NMR (200 MHz, thf-d_8, 293 K, δ/ppm, *J*/Hz): 6.76 (d, 2 H, $C_6H_3Pr^i_2$, *J* = 6.5), 6.54 (d, 2 H, $C_6H_3Pr^i_2$, *J* = 6.8), 6.02 (pst, 2 H, $C_6H_3Pr^i_2$), 4.77 (pst, 2 H, naphthalene), 3.95 (spt, 2 H, $CH(CH_3)_2$, *J* = 6.3), 3.80-3.50 (br m, thf), 3.32 (d, 2 H, naphthalene, *J* = 7.0), 3.20-2.90 (spt, 2 H, $CH(CH_3)_2$, *J* = 6.3 overlapping with d, 2 H, naphthalene), 2.0-1.5 (br m, thf), 1.56 (d, 6 H, $CH(CH_3)_2$, *J* =

6.3), 1.10 (d, 6 H, CH(CH_3)$_2$, *J* = 6.3), 1.00 (d, 6 H, CH(CH_3)$_2$, *J* = 6.3), 0.74 (d, 6 H, CH(CH_3)$_2$, *J* = 6.3). IR (Nujol): 1667 w, 1642 w, 1579 s, 1562 w, 1521 m, 1413 w, 1402 w, 1355 m, 1311 m, 1247 s, 1189 w, 1173 w, 1137 m, 1104 w, 1078 w, 1054 s, 1035 m, 979 m, 935 w, 916 w, 902 s, 877 w, 844 w, 836 w, 814 w, 786 m, 750 m, 731 m, 687 m, 665 m, 620 w, 565 m, 521 m cm^{-1}.

[(dpp-bian)$_2^{4-}$Yb$_3$K$_2$(thf)$_8$] (9). Iodine (0.25 g, 1.0 mmol) was added to ytterbium shavings (10 g) in thf (30 mL). The mixture was stirred at ambient temperature till the color of iodine completely disappeared. Then the light yellow solution was decanted and the metal was washed with thf (3×30 mL). A solution of dpp-bian (0.5 g, 1.0 mmol) and iodine (0.13 g, 0.5 mmol) in thf (30 мл) was added to activated ytterbium. The reaction mixture was stirred at reflux within *ca*. 24. The resulted brown solution was decanted from ytterbium and added *in situ* to potassium metal 0.4 g (10.0 mmol). The mixture was stirred at ambient temperature within *ca*. 20 hours. Concentration of the mother liquor under vacuum resulted complex **9** as dark crystals (0.75 g, 65 %). Mp. 315 °C. Found: C, 57.21; H, 6.11. $C_{112}H_{160}K_2N_4O_{10}Yb_3$ (2319.75). Calculated: C, 57.99; H, 6.95. ^{1}H NMR (400 MHz, thf-d$_8$, 293 K, δ/ppm, *J*/Hz): 6.85 (br s, 2 H, C$_6H_3$Pr$^i_2$, *J* = 7.0), 6.68 (br d, 1 H, C$_6H_3$Pr$^i_2$, *J* = 7.3), 6.51 (d, 1 H, C$_6H_3$Pr$^i_2$, *J* = 7.3), 6.26 (dd, 1 H, C$_6H_3$Pr$^i_2$, *J* = 7.0, *J* = 7.3), 6.06 (dd, 1 H, C$_6H_3$Pr$^i_2$, *J* = 7.3, *J* = 7.5), 5.23 (dd, 1 H, naphthalene, *J* = 7.3, *J* = 7.5), 4.98 (dd, 1 H, naphthalene, *J* = 7.0, *J* = 7.5), 4.01 (br s, 1 H, C*H*(CH$_3$)$_2$), 3.84-3.42 (br m, thf, overlapping with 2 H naphthalene), 3.40 (sept, 1 H, C*H*(CH$_3$)$_2$, *J* = 6.5), 3.36 (br s, 1 H, naphthalene), 3.26 (br s, 1 H, C*H*(CH$_3$)$_2$), 3.13 (br d, 1 H, naphthalene, *J* = 7.5), 2.99 (br m, 1 H, C*H*(CH$_3$)$_2$), 2.0-1.5 (br m, thf overlapping with 3 H, CH(CH_3)$_2$), 1.45 (br d, 3 H, CH(CH_3)$_2$), 1.19 (br d, 3 H, CH(CH_3)$_2$, *J* = 6.5), 1.12 (br d, 3 H, CH(CH_3)$_2$, *J* = 6.5), 1.01 (br d, 3 H, CH(CH_3)$_2$, *J* = 6.5), 0.93-0.55 (br s, 9 H, CH(CH_3)$_2$). IR (Nujol): 2727 w, 2675 w, 1664 w, 1642 w, 1573 m, 1305 m, 1266 w, 1242 w, 1195 w, 1167 w, 1156 m, 1104 w, 1073 m, 1051 w, 1032 m, 974 m, 935 w, 918 w, 899 m, 872 w, 844 m, 778 m, 664 w, 609 w, 562 m, 524 w, 507 w, 488 w, 463 w cm^{-1}.

[(dpp-bian)$^{4-}$Tm^{3+}Na$^+$(thf)]$_2$ (**10**). A solution of dpp-bian (0.5 g, 1.0 mmol) and 1,2-dibromostilbene (0.17 g, 0.5 mmol) in thf (40 mL) was added to thulium shavings (10 g). Stirring of the mixture resulted in a deep blue solution. The solution was decanted and stirred with sodium metal (0.5 g, 22 mmol) during *ca*. 8 hours. The reaction mixture color changed gradually from deep blue to green and finally to red-brown. The precipitated sodium bromide was separated by centrifugation. The residual solid left after evaporation of thf was dissolved in toluene (40 mL). Complex **10** was isolated from concentrated toluene solution as dark crystals (0.35 g, 46 %). Mp. ≥ 230 °C. Found: C, 62.24; H, 5.93. $C_{80}H_{96}N_4Na_2O_2Tm_2$ (1529.44). Calculated: C, 62.82, H, 6.33. IR (Nujol): 1648 w, 1592 s, 1567 s, 1543 w, 1435 w, 1418 w, 1338 m, 1313 m, 1283 w, 1264 w, 1244 w, 1195 m, 1173 w, 1150 s, 1126 m, 1109 w, 1057 s, 996 m, 924 m, 896 m, 836 w, 783 m, 761 m, 662 w, 648 w, 601 w, 568 w, 485 w cm^{-1}.

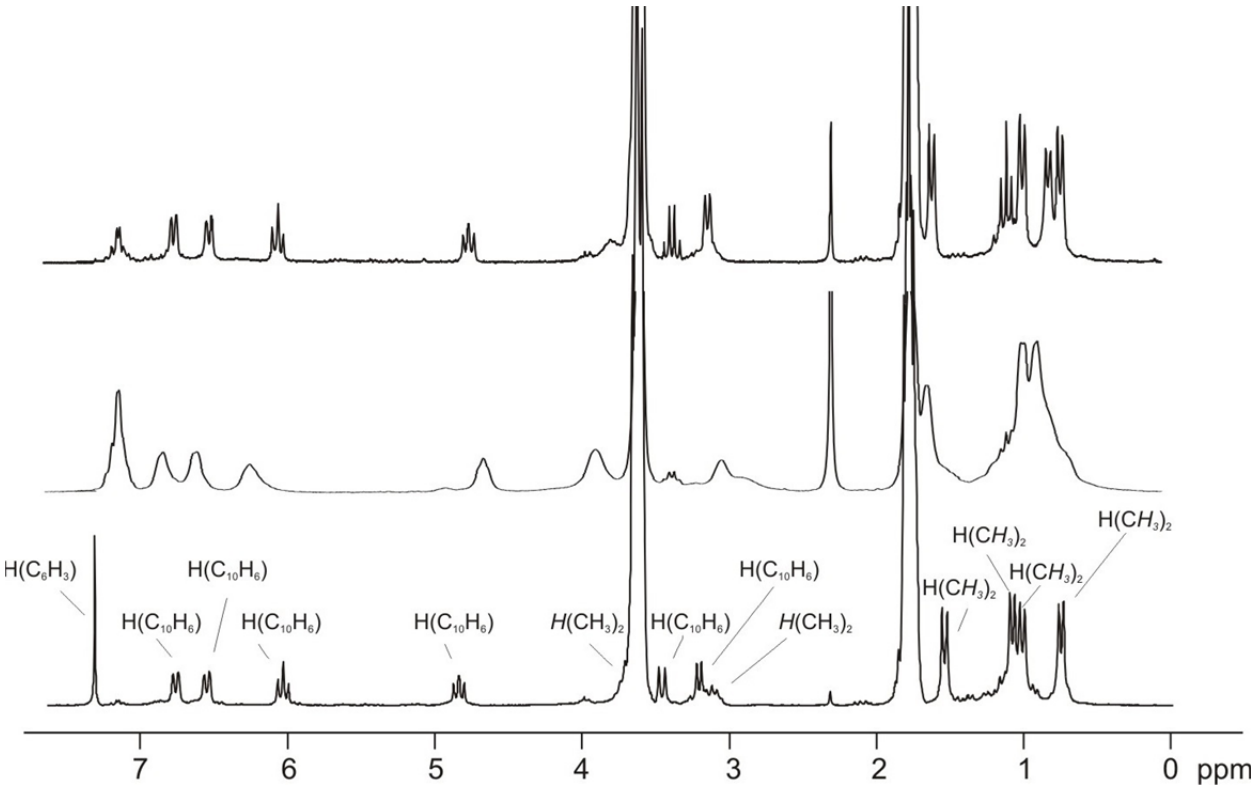

Figure S1 ^{1}H NMR spectra of **4** (top), **3** (middle) and **5** (bottom) in thf-d_8. The signals of thf molecules at 3.59 and 1.73 ppm are cut-off for clarity.

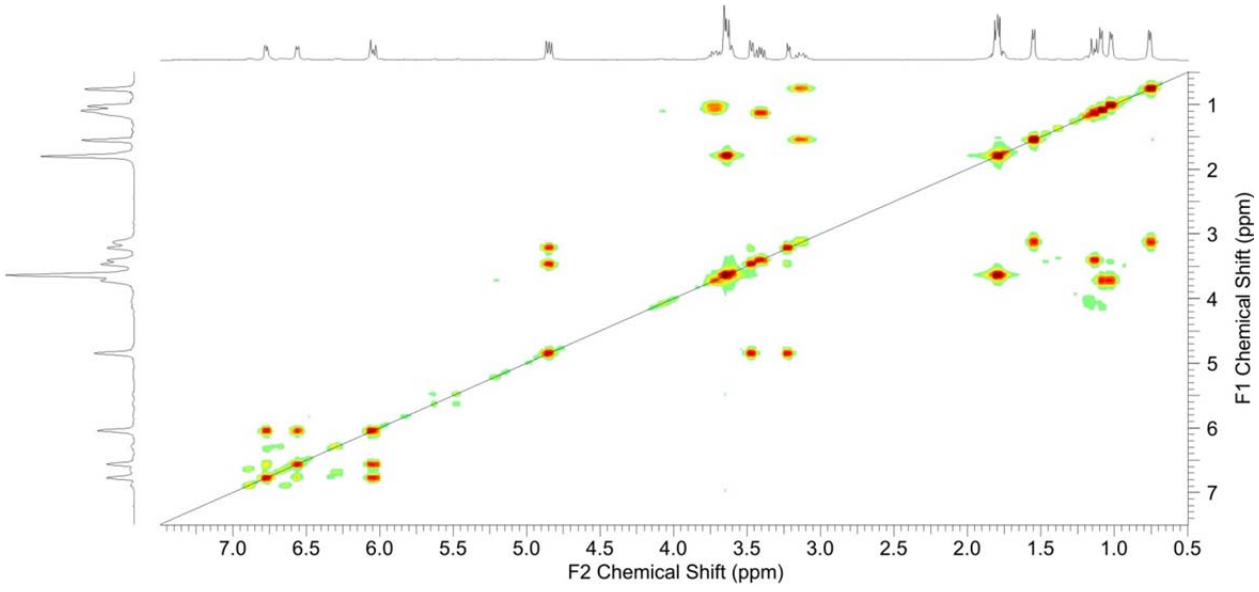

Figure S2 ^{1}H-^{1}H COSY NMR spectrum of **5** in thf-d_8.

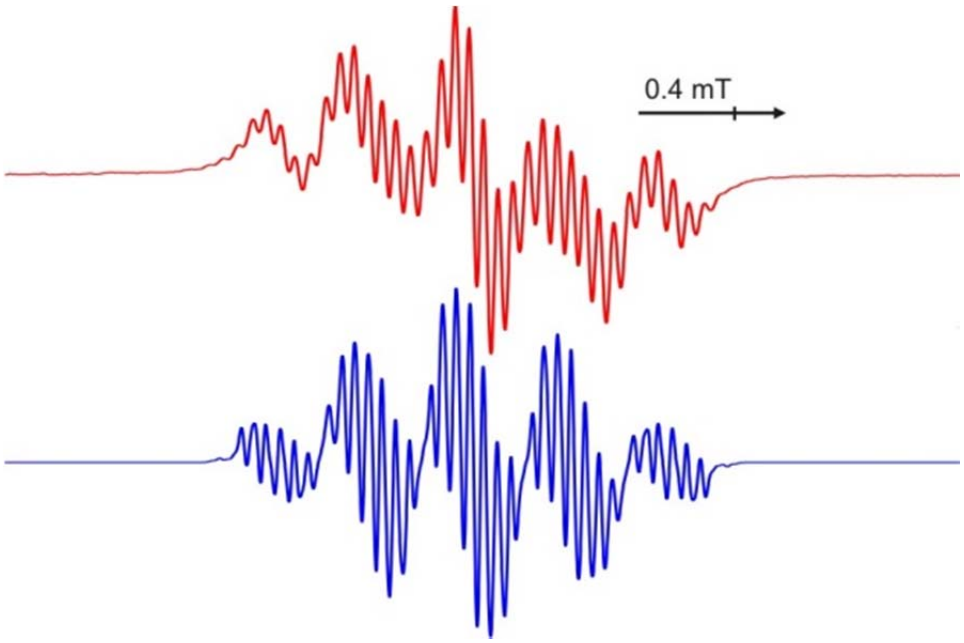

Figure S3 ESR spectrum of complex **7** (thf, 298 K); red - experimental; blue - simulated: g_i = 2.00406; a_H = 0.482 (1×^{1}H), a_H = 0.427 (1×^{1}H), a_H = 0.376 (1×^{1}H), a_H = 0.362 (1×^{1}H), a_H = 0.060 (1×^{1}H), a_H = 0.036 (1×^{1}H), a_N = 0.005 (2×^{14}N), a_K = 0.060 (1×^{39}K), a_{Yb} = 0.05 (1×^{173}Yb), a_{Yb} = 0.18 (1×^{171}Yb) mT.

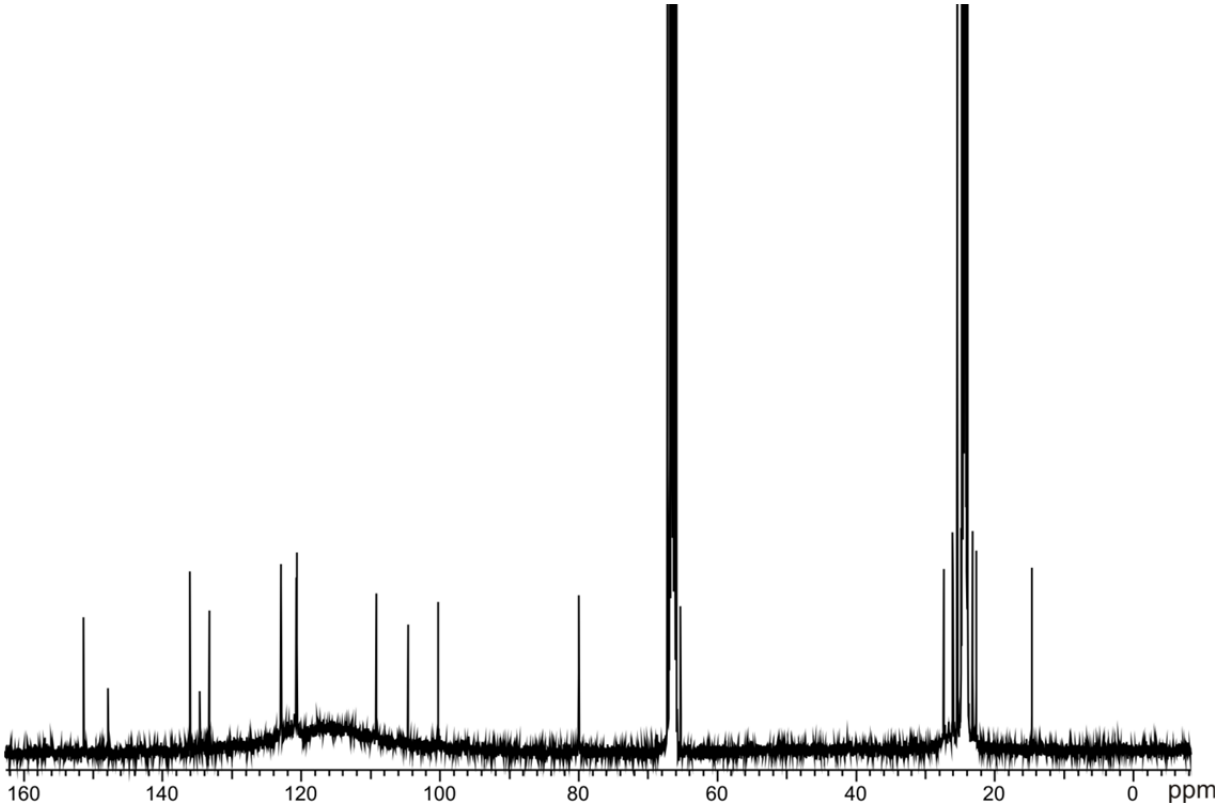

Figure S4 ^{13}C NMR spectrum of **5** in thf-d_8

X-ray Crystallography

The X-ray data for **3**, **9** and **10** were collected at T = 100(2) K on *Bruker D8 Quest* (**3**, **9**) and *Bruker Smart Apex* (**10**) diffractometers (MoKα-radiation, ω-scan technique, λ = 0.71073 Å). The intensity data were collected and integrated by *APEX2* and *SMART* software.[1] The structures were solved by dual space and direct methods and were refined on F^2 using SHELX.[2] All non-hydrogen atoms were found from differential Fourier maps and were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined isotropically in the riding model with $U_{iso}(H)$ = 1.2$U_{eq}(C)$ ($U_{iso}(H)$ = 1.5$U_{eq}(C)$ for CH_3-groups). SADABS[3] were used to perform absorption corrections. One of thf molecules coordinated by Na ion in **3** is disordered over two sites. The K(1) and Yb(2) ions in **9** are disordered with each other with a population of 50 %. Crystallographic data and structures refinement details for complexes **3**, **9** and **10** are presented in ***Table S1***; selected bond length and angles in ***Table S2, S3*** *and* ***S4***. CCDC-1859896 (**3**), 1859894 (**9**), 1859895 (**10**) contain the supplementary crystallographic data for this paper. These data can also be obtained free of charge at ccdc.cam.ac.uk/structures (Cambridge Crystallographic Data Centre).

[1] Bruker (2012). *SMART*, *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

[2] *a)* G.M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3; *b)* G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.

[3] L. Krause, R. Herbst-Irmer, G.M. Sheldrick, D. Stalke, *J. Appl. Cryst.*, 2015, **48**, 3.

Table S1. Crystallographic data and structures refinement details for complexes **3**, **9**, **10.**

	3	**9**	**10**
Formula	$C_{112}H_{160}Ca_2N_4Na_4O_{10}$	$C_{112}H_{160}K_2N_4O_{10}Yb_3$	$C_{80}H_{96}N_4Na_2O_2Tm_2$
M_r	1894.55	2319.75	1529.44
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P–1*	*P–1*	$P2_1/n$
a, Å	13.0748(9)	13.294(2)	13.694(3)
b, Å	13.2572(9)	13.787(3)	16.730(4)
c, Å	15.9107(10)	15.741(3)	14.700(3)
α, °	79.7990(10)	105.839(2)	90
β, °	85.2460(10)	92.357(2)	91.656(6)
γ, °	69.1460(10)	112.705(2)	90
V, Å3	2535.9(3)	2525.5(8)	3366.3(13)
Z	1	1	2
d_{calc}, Mg/m3	1.241	1.525	1.509
μ, mm-1	0.191	2.898	2.683
ϑ range, °	2.49–30.37	2.34–24.84	2.00 to 28.79
HKL ranges	$-18 \le h \le 18$ $-18 \le k \le 18$ $-22 \le l \le 22$	$-15 \le h \le 15$ $-16 \le k \le 16$ $-18 \le l \le 18$	$-18 \le h \le 18$ $-22 \le k \le 22$ $-19 \le l \le 19$
Collected (unique) refls.	35764 (15181)	17480 / 8685	33522 / 8741
R_{int}	0.0322	0.0535	0.0692
Max. / min. transm.	0.971 / 0.845	0.674 / 0.444	0.666 / 0.521
Data / restraints / parameters	15181 / 12 / 623	8685 / 6 / 610	8741 / 0 / 414
GOF on F^2	1.018	1.040	1.047
R_1 ($I>2\sigma(I)$)	0.0535	0.0498	0.0468
wR_2 (all data)	0.1395	0.1201	0.1202
Largest diff. peak and hole, e/A^3	0.96 / –0.67	2.54 / –1.05	3.06 / –1.34

Table S2. Selected bond lengths (Å) and angles (°) for complex **3**.

Bond lengths (Å)			
Ca(1)–N(1)	2.375(2)	Na(1)–C(2)	2.522(2)
Ca(1)–N(2)	2.339(2)	Na(1)–C(3)	2.536(2)
Ca(1)–O(1)	2.378(2)	Na(2)–C(10)’	2.587(2)
Ca(1)–C(6)’	2.739(2)	Na(2)–C(11)’	2.679(2)
Ca(1)–C(7)’	2.704(2)	N(1)–C(1)	1.423(2)
Na(1)–N(1)’	2.480(2)	N(2)–C(2)	1.422(2)
		N(1)–Na(1)’	2.480(2)
		C(1)–C(2)	1.443(2)
Angles (°)			
N(1)–Ca(1)–N(2)	80.01(4)	N(2)–Ca(1)–O(1)	87.19(4)
N(1)–Ca(1)–O(1)	118.04(4)		

Table S3. Selected bond lengths and angles for complex **9**.

Bond lengths (Å)			
Yb(1)–N(1)	2.332(5)	Yb(2)–C(2)	2.393(7)
Yb(1)-N(2)	2.357(6)	Yb(2)–C(3)	2.402(7)
Yb(1)–O(1)	2.362(5)	Yb(2)–N(1)’	2.412(6)
Yb(1)–C(6)’	2.699(7)	Yb(2)–N(2)	2.705(6)
Yb(1)–C(7)’	2.658(7)	Yb(2)–C(1)’	2.720(7)
Yb(1)–C(8)	2.741(7)	N(1)–C(1)	1.430(9)
K(1)–C(3)	2.817(7)	N(2)–C(2)	1.416(8)
K(1)–N(2)’	2.868(6)	C(1)–C(2)	1.43(2)
Angles (°)			
O(1)–Yb(1)–N(1)	112.0(2)	N(1)–Yb(1)–N(2)	80.5(2)
O(1)–Yb(1)–N(2)	88.0(2)		

Table S4. Selected bond lengths and angles for complex **10**.

Bond lengths (Å)			
Tm(1)–N(1)	2.188(4)	Na(1)–C(5)	2.488(6)
Tm(1)–N(2)	2.228(4)	Na(1)–C(6)	2.710(5)
Tm(1)–O(1)	2.316(3)	Na(1)–N(2)	2.722(5)
Tm(1)–C(11)	2.602(5)	N(1)–C(1)	1.429(6)
Tm(1)–C(12)	2.619(5)	N(2)–C(2)	1.440(6)
		C(1)–C(2)	1.443(7)
Angles (°)			
N(1)–Tm(1)–O(1)	83.7(2)	N(1)–Tm(1)–N(2)	84.9(2)
N(2)–Tm(1)–O(1)	110.9(2)		