SUPPLEMENTARY MATERIAL

Europium and ytterbium complexes with o-iminoquinonato ligands: synthesis, structure, and magnetic behavior

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Content:

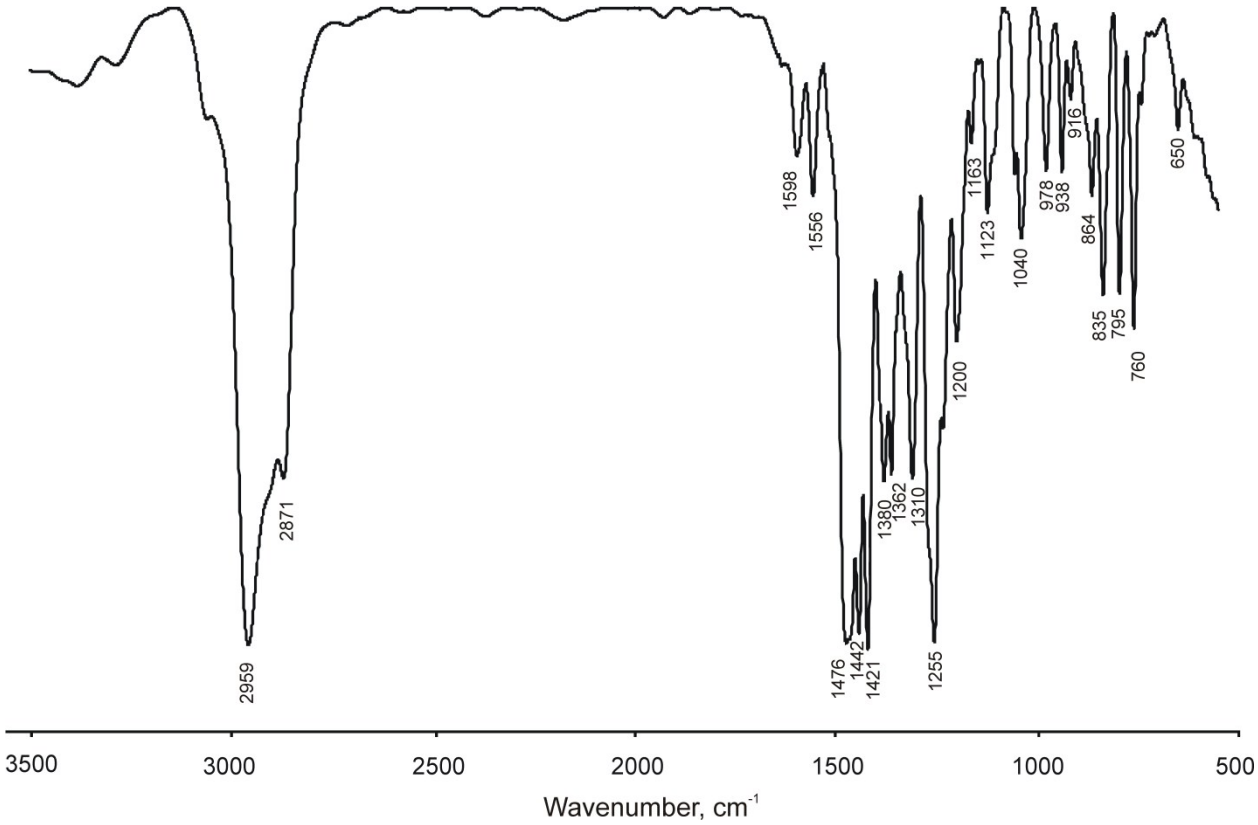

Figure S1. IR spectrum of **1**

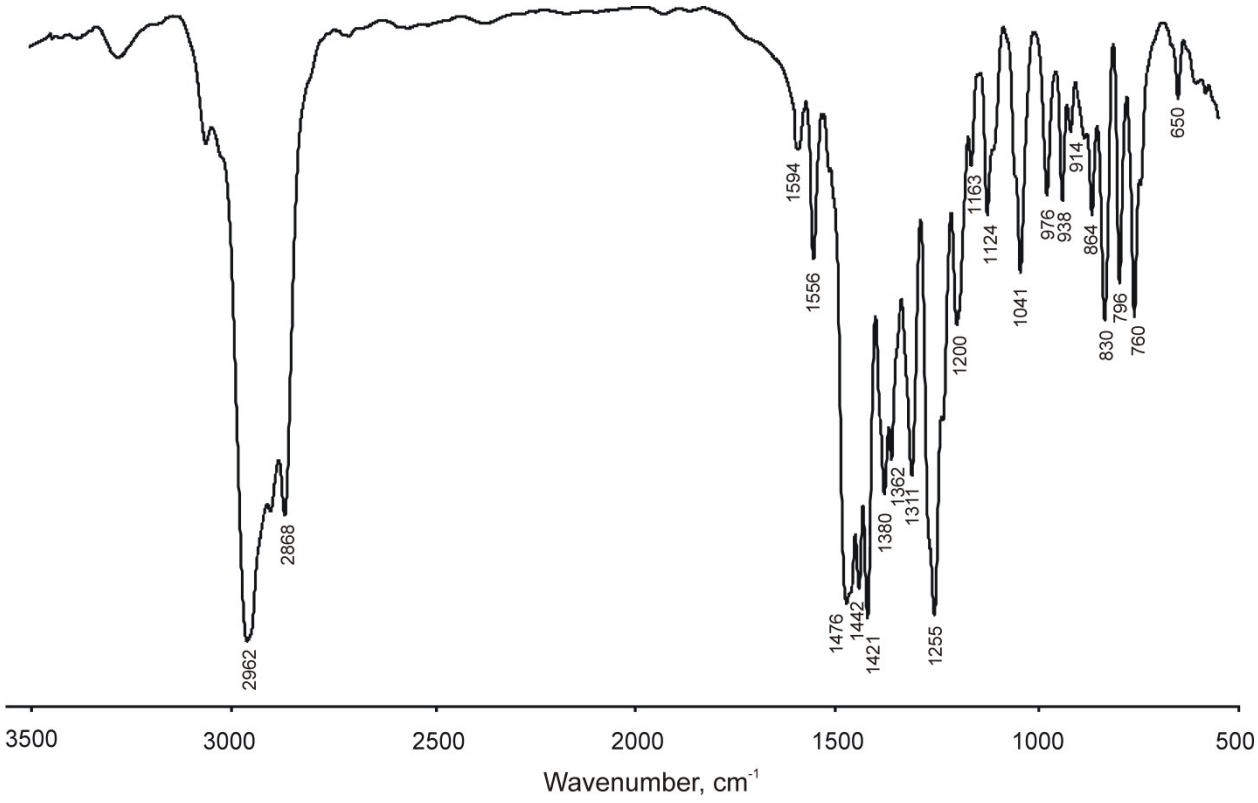

Figure S2. IR spectrum of **2**

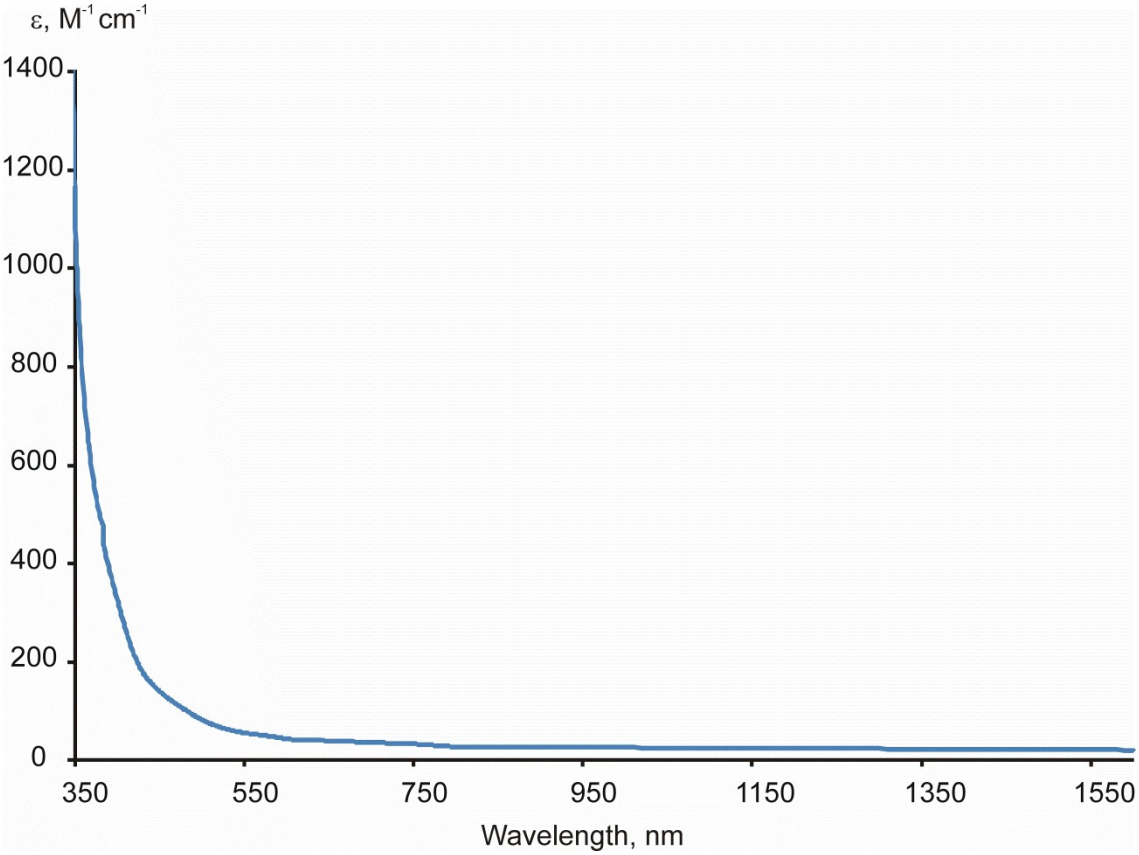

Figure S3. Electronic absorption spectrum of **1** recorded at room temperature in THF solution

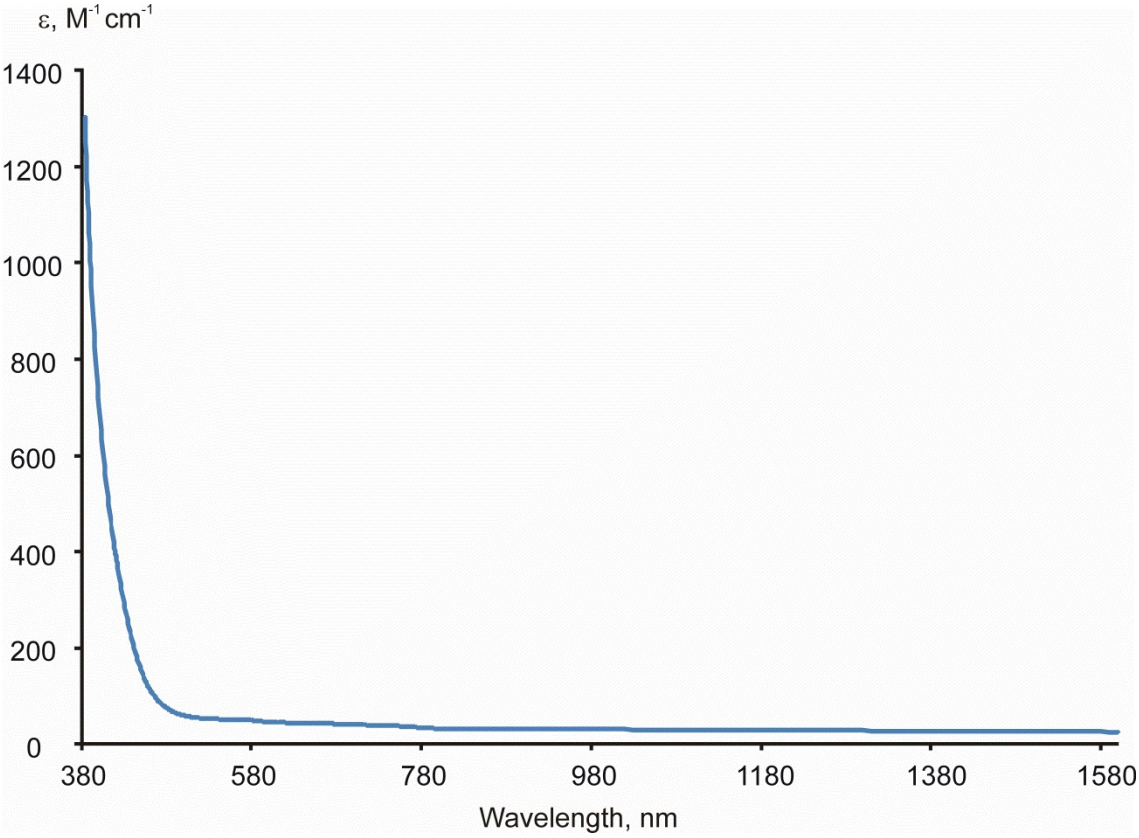

Figure S4. Electronic absorption spectrum of **2** recorded at room temperature in THF solution

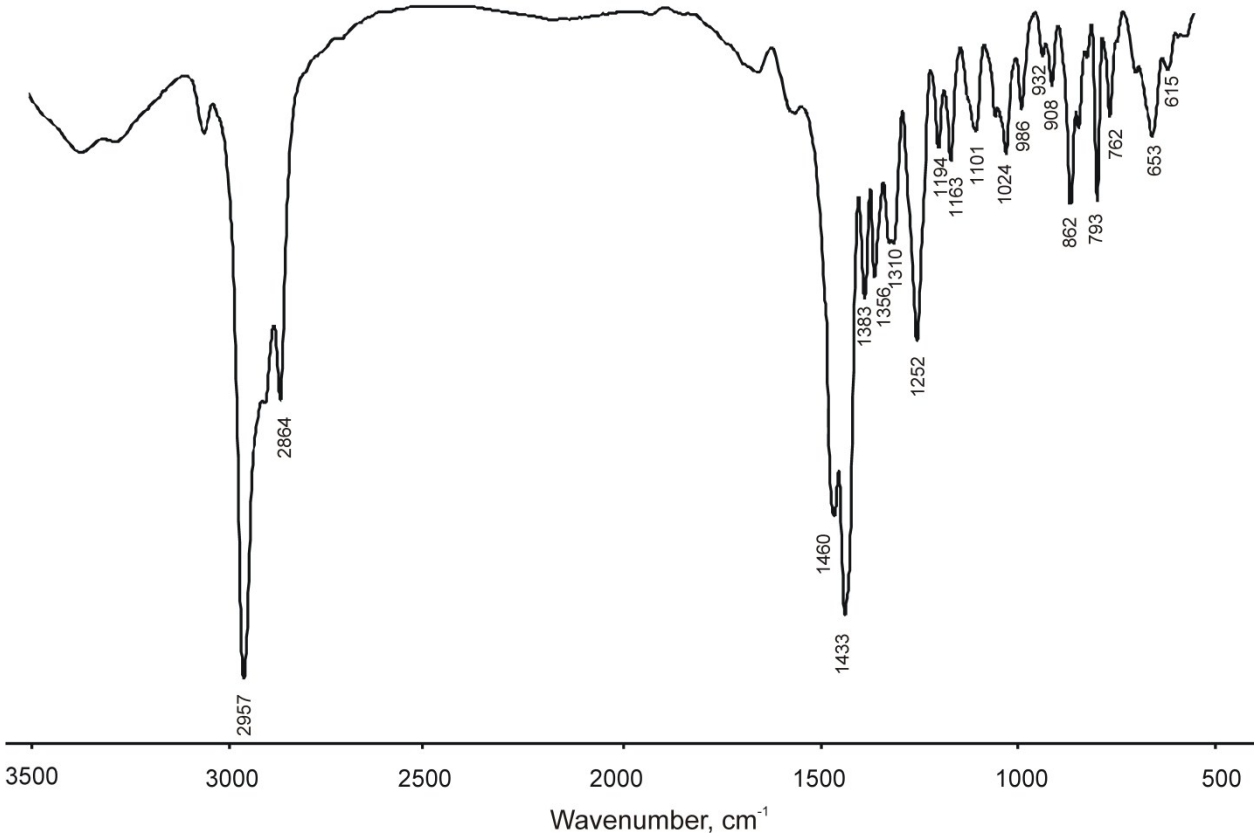

Figure S5. IR spectrum of **3**

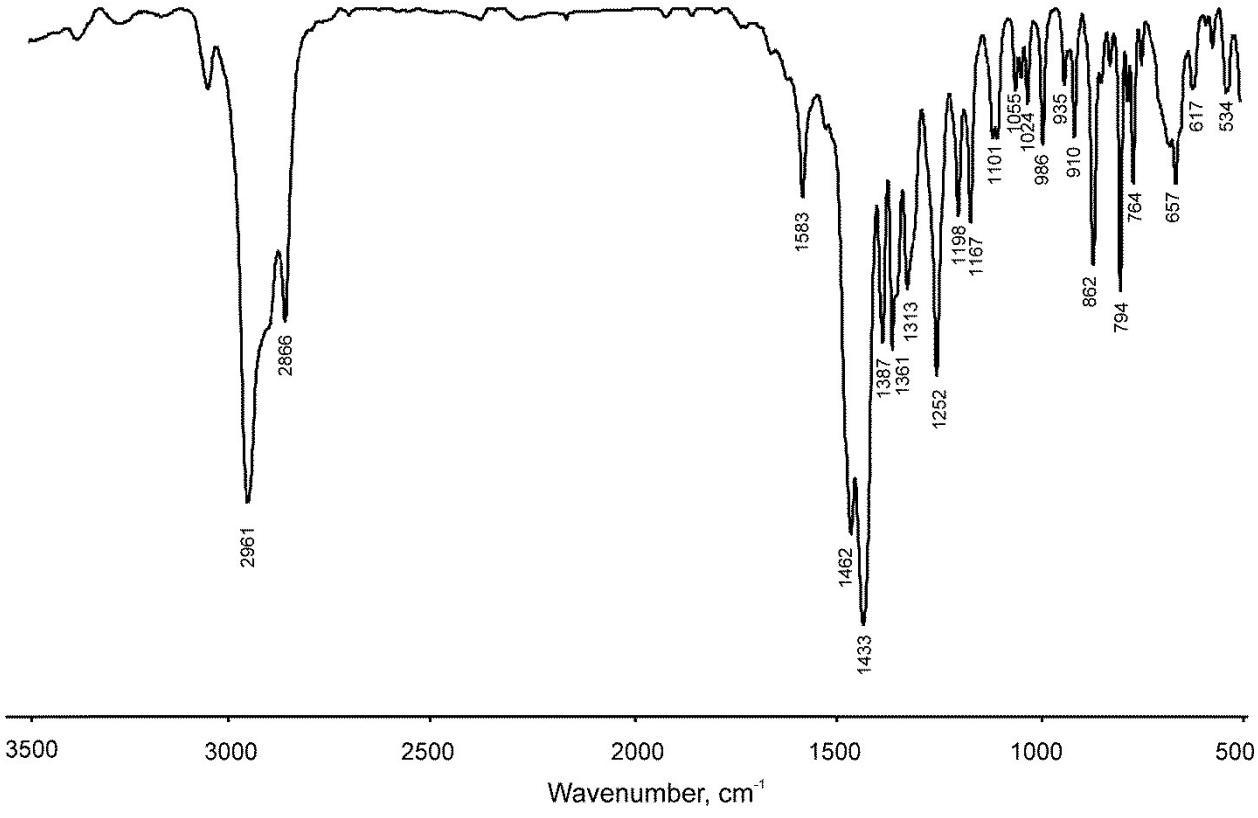

Figure S6. IR spectrum of **3-*dimer***

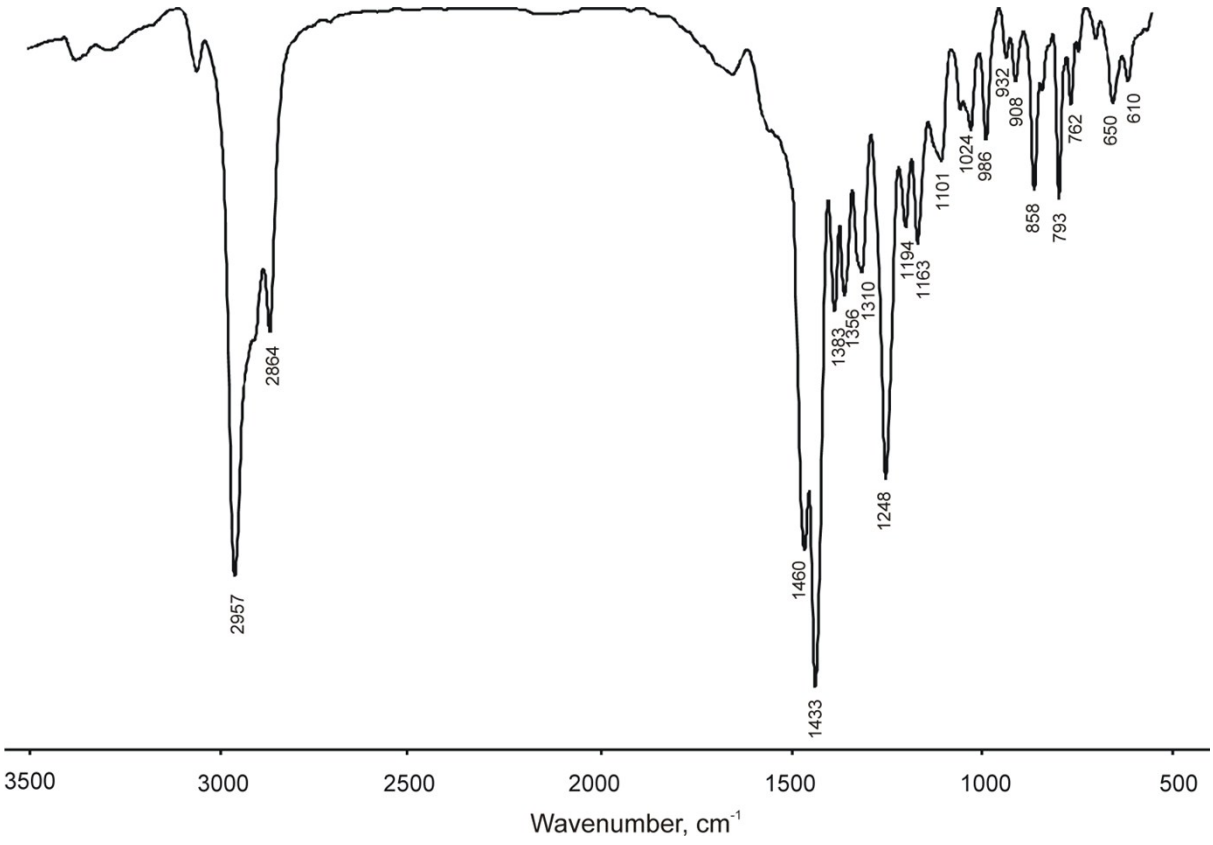

Figure S7. IR spectrum of **4**

Cyclic voltammetry

CV measurements were carried out in THF solution at ambient temperature using Epsilon ES-USB-V200 potentiostate equipped with a three-electrode cell C3 under the following conditions: working electrode – glassy carbon, reference electrode - $Ag/AgNO_3$, 0.01 M (CH_3CN), auxiliary electrode – Pt, background electrolyte - NBu_4BF_4, 0.2 M, sample concentration - 1 μM**,** scanning rate - 100 mV/s. Peak potentials are given vs. Fc/Fc^+.

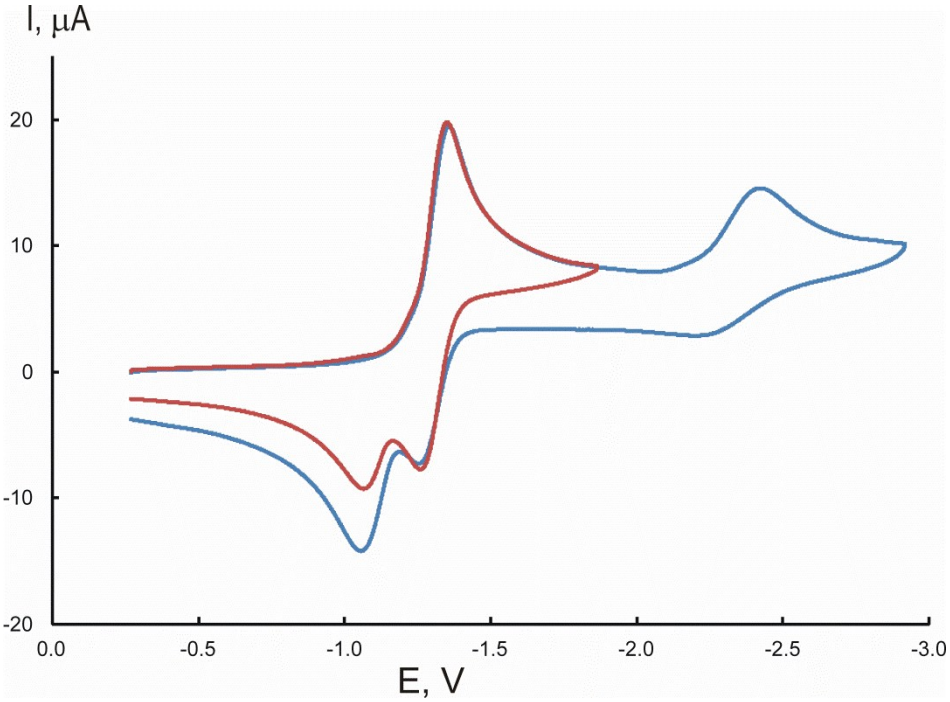

Figure S8. Cyclic voltammogram of dpp-IQ.

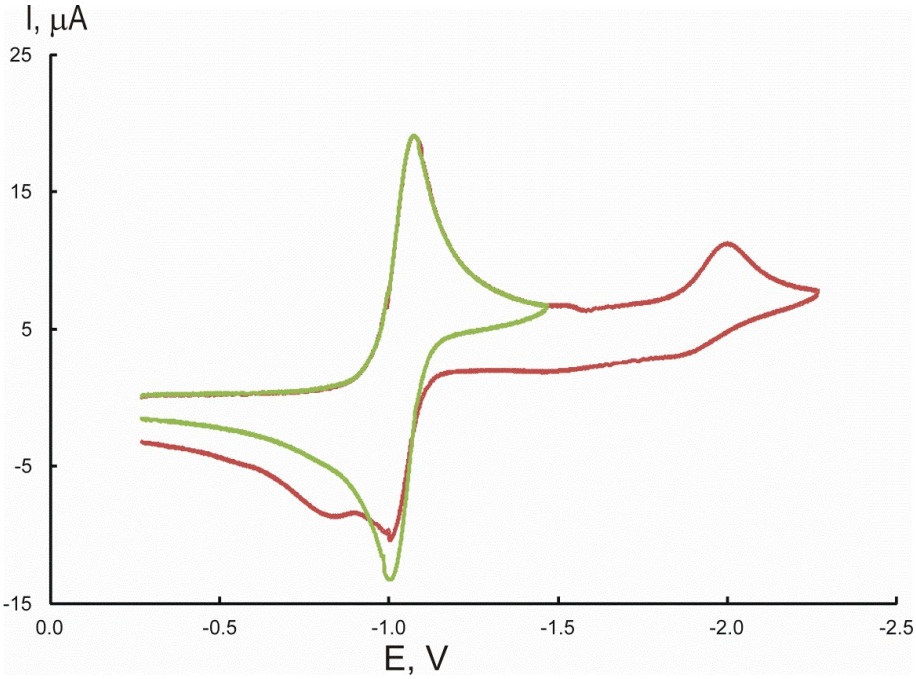

Figure S9. Cyclic voltammogram of 3,6-Q.

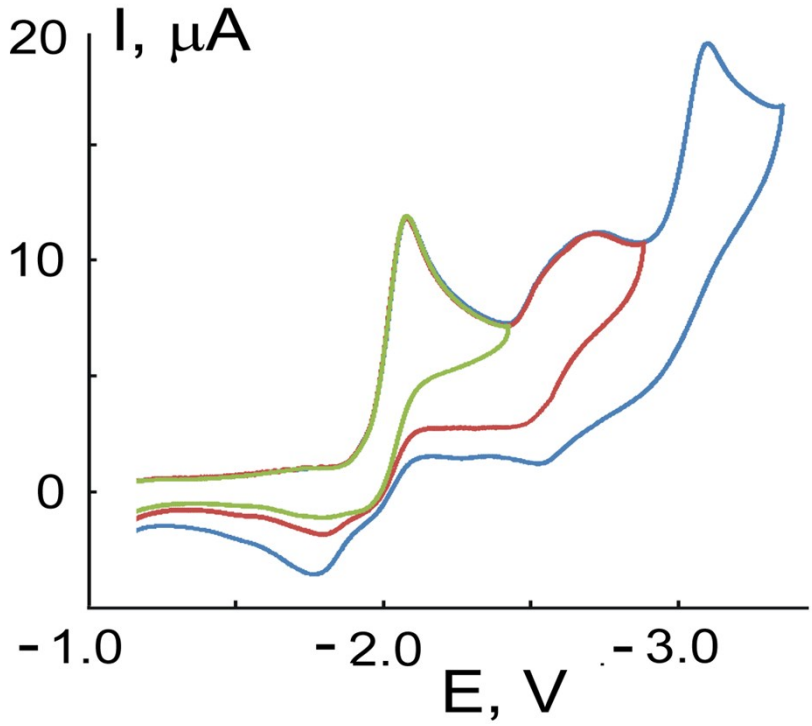

Figure S10. Cyclic voltammogram of dpp-BIAN.

The first reduction peak potentials, V vs. Fc/Fc^+.

3,6-Q	-1.07
dpp-IQ	-1.34
dpp-BIAN	-2.07

Table S1. Comparable distances Ln-O and Ln-N

Compound	bond	bond length, Å	ref.
$[(Eu^{III}Cp^*)(Eu^{II}\cdot THF)_2(3,6\text{-}Cat)_3]$	Eu^{II}–O	2.429(3)	1
		2.439(2)	
		2.457(2)	
		2.457(3)	
$[(dpp\text{-}BIAN^{2-})Yb^{II}(dme)_2]$	Yb^{II}–N	2.347(2)	2
		2.363(2)	
$[Yb^{II}(L^1)_2(THF)_2]$[a]	Yb^{II}–N	2.386(2)	3
$[Yb^{II}(L^1)_2(dme)]$[a]	Yb^{II}–N	2.353(4)	4
$[(dpp\text{-}BIAN^{2-})Eu^{II}(dme)_2]$	Eu^{II}–N	2.445(3)	5
		2.475(3)	
$[(tms\text{-}BIAN^{2-})Eu^{II}(THF)_2]$[b]	Eu^{II}–N	2.563(2)	6
		2.597(2)	
$[Eu^{II}(L^2)_2(THF)_2]$[c]	Eu^{II}–N	2.498(2)	4
$[Eu^{II}(L^1)_2(dme)]$[a]	Eu^{II}–N	2.479(1)	4
$[(Yb^{III}Cp^*)_2(3,6\text{-}Cat)_2]$	Yb^{III}–O	2.1285(18)	1
		2.2264(19)	
$[(Eu^{III}Cp^*)(Eu^{II}\cdot THF)_2(3,6\text{-}Cat)_3]$	Eu^{III}–O	2.280(2)	1
		2.289(2)	
		2.300(2)	
		2.311(2)	
$[(dpp\text{-}BIAN^{2-})Yb^{III}(bipy)(bipy)^{1-}]$	Yb^{III}–N	2.215(3)	7
		2.239(3)	
$[(dpp\text{-}BIAN^{1-})Yb^{II}(dme)_2]^+$ $[(dpp\text{-}BIAN^{2-})_2Yb^{III}]^-$	Yb^{III}–N	2.194(3)	8
		2.198(3)	
		2.191(2)	
		2.206(2)	
$[Yb^{III}(L^1)_2(\mu\text{-}OMe)]_2$[a]	Yb^{III}–N	2.250(3)	3
		2.245(3)	
$[Yb^{III}(L^2)_2(OPh)(THF)]$[c]	Yb^{III}–N	2.250(5)	3
		2.247(5)	

[a] L^1H = N-(2-methoxyphenyl)-N-(trimethylsilyl)amine; [b] tms-BIAN = 1,2-bis(trimethylsilylimino)acenaphthene; [c] L^2H = N-(2-phenoxyphenyl)-N-(trimethylsilyl)amine

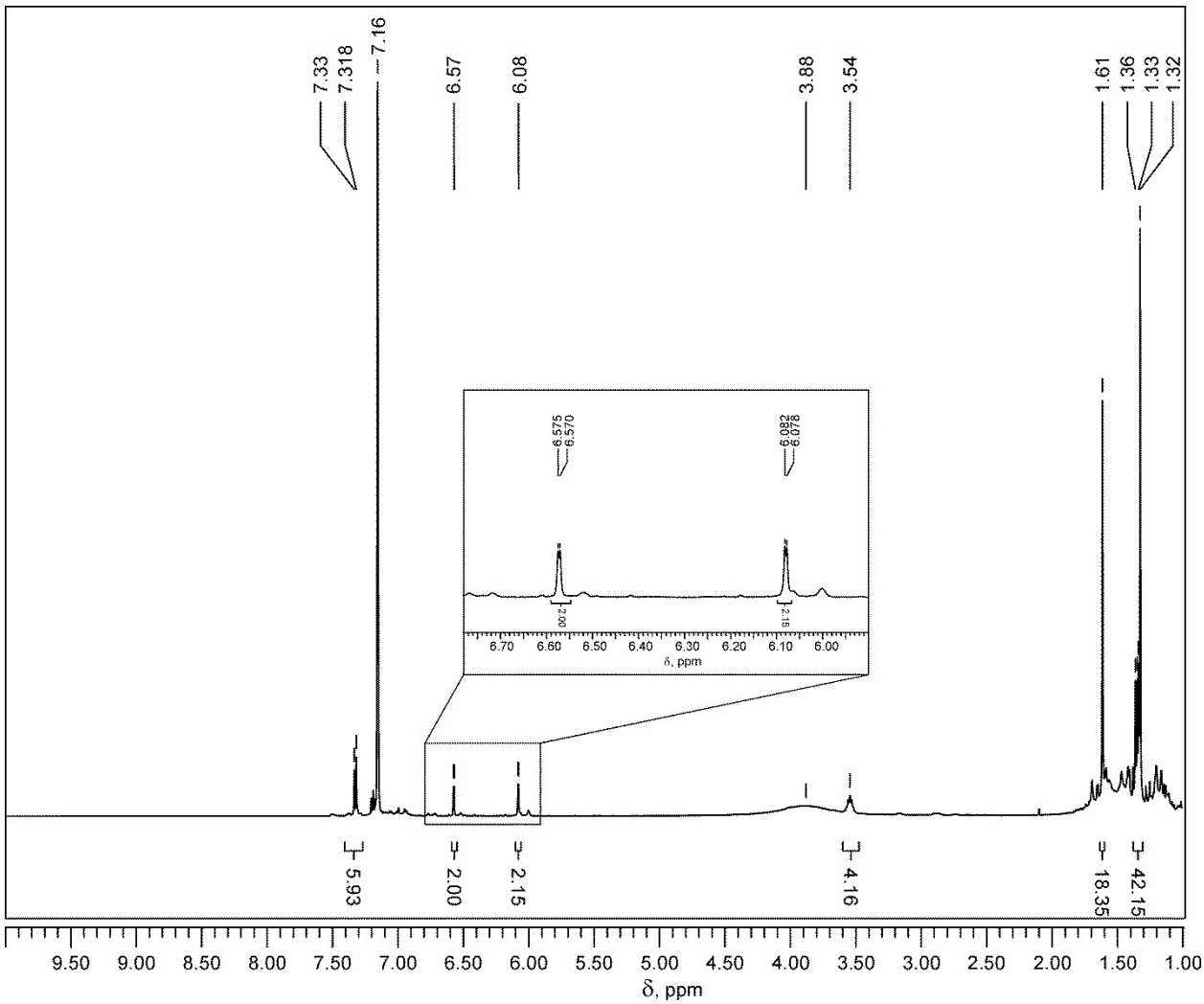

Figure S11. ^{1}H NMR of **1**.

^{1}H NMR (500 MHz, d_6-benzene): 1.32 (s, 18 H, 2 tBu), 1.33 (d, $^{3}J(H,H)$ = 6.8 Hz, 12H, CH_3 of iPr), 1.36 (d, $^{3}J(H,H)$ = 6.8 Hz, 12H, CH_3 of iPr), 1.61 (s, 18 H, 2 tBu), 1.69 (br.m., 4H, THF), 3.54 (sept., $^{3}J(H,H)$ = 6.8 Hz, 4H, CH of iPr), 3.88 (br.s., 4H, THF), 6.08 (d, $^{4}J(H,H)$ = 2.1 Hz, 2H, C_6H_1 arom.), 6.57 (d, $^{4}J(H,H)$ = 2.1 Hz, 2H, C_6H_1 arom.), 7.27-7.40 (m, 6H, C_6H_3 arom.).

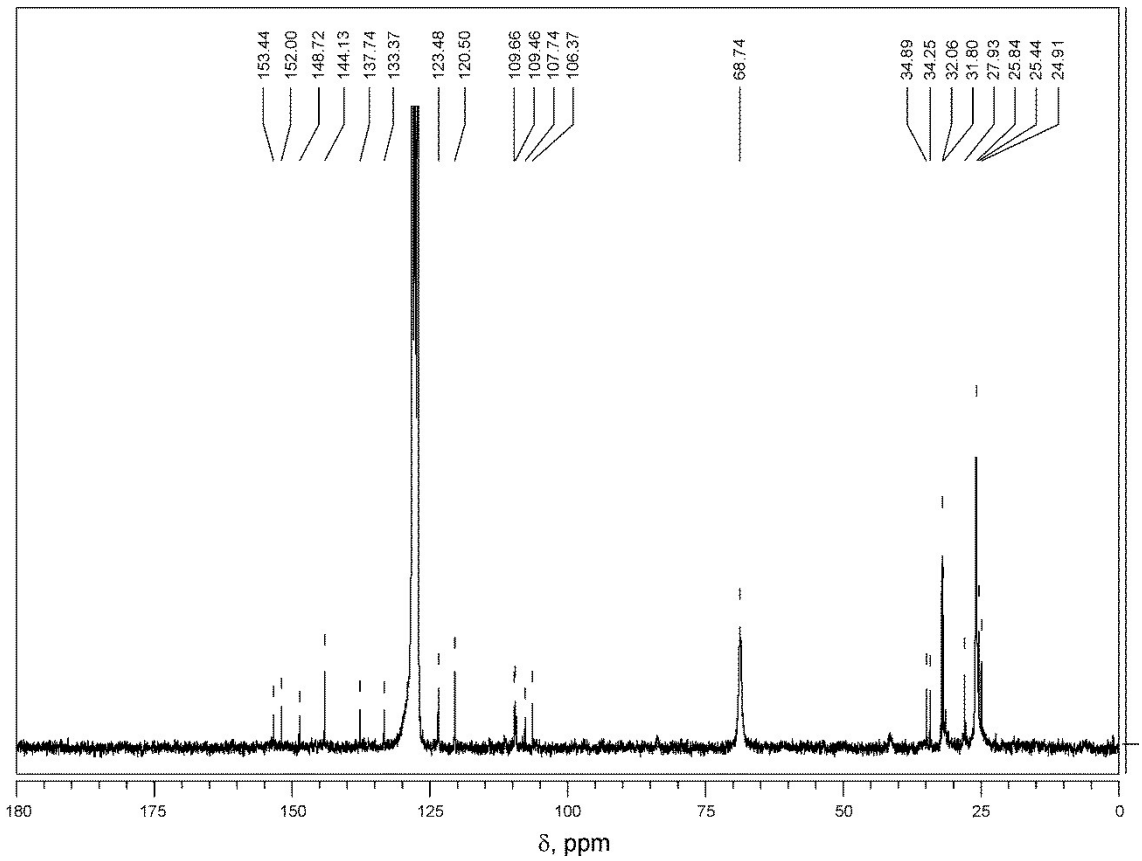

Figure S12. $^{13}C\{^{1}H\}$ NMR of **1**.

^{13}C NMR (50 MHz, d_6-benzene): 24.91 (CH_3 of iPr), 25.44 (CH_3 of iPr), 25.84 (THF), 27.93 (CH of iPr), 31.80 (CH_3 of tBu), 32.06 (CH_3 of tBu), 34.25 (C of tBu), 34.89 (C of tBu), 68.74 (THF), 106.37 (CH arom.), 107.74 (CH arom.), 109.45 (CH arom.), 109.66 (CH arom.), 120.50 (C(tBu) arom.), 123.48 (CH arom.), 133.37 (C arom.), 137.74 (C arom.), 144.13 (C(tBu) arom.), 148.72 (C arom.), 152.00 (C(N) arom.), 153.44 (C(O) arom.).

Evaluation of the effective magnetic moments by Evans Method

NMR spectra for Evans Method were recorded in THF with a Bruker Avance DPX-200.

$\chi_{mass} = 3\Delta f/4\pi fm + \chi_0$

$\chi_0(THF) = -0.6389*10^{-6}$ cm^3g^{-1}

f = 200 MHz

m – concentration in g/cm^3

Initial data and calculation for complex **3**

T = 302 K

M = 1076.42 g mol^{-1}

Δf_1= 79.4 Hz (the first THF multiplet)

Δf_2= 77.0 Hz (the second THF multiplet)

Δf_{av}= 78.2 Hz

m = 0.0109g/1.06cm^3 = 0.010283 g/cm^3

$\chi_{mass} = 8.44 \cdot 10^{-6}$ cm^3g^{-1}

$\mu_{eff} = (8\ \chi_{mol}T)1/2$

$\chi_{mol} = \chi_{mass}$ M

μ_{eff} = 4.69±0.04 μB

Initial data and calculation for complex **4**

T = 303

M = 1055.33 g mol^{-1}

Δf_1= 101.5 Hz (the first THF multiplet)

Δf_2= 99.2 Hz (the second THF multiplet)

Δf_{av}= 100.4 Hz

m = 0.0194g/1.113 cm^3 = 0.01743 g/cm^3

$\chi_{mass} = 6.24 \cdot 10^{-6}$ cm^3g^{-1}

$\mu_{eff} = (8\ \chi_{mol}T)1/2$

$\chi_{mol} = \chi_{mass}$ M

μ_{eff} = 3.99±0.03 μB

Additional magnetic data

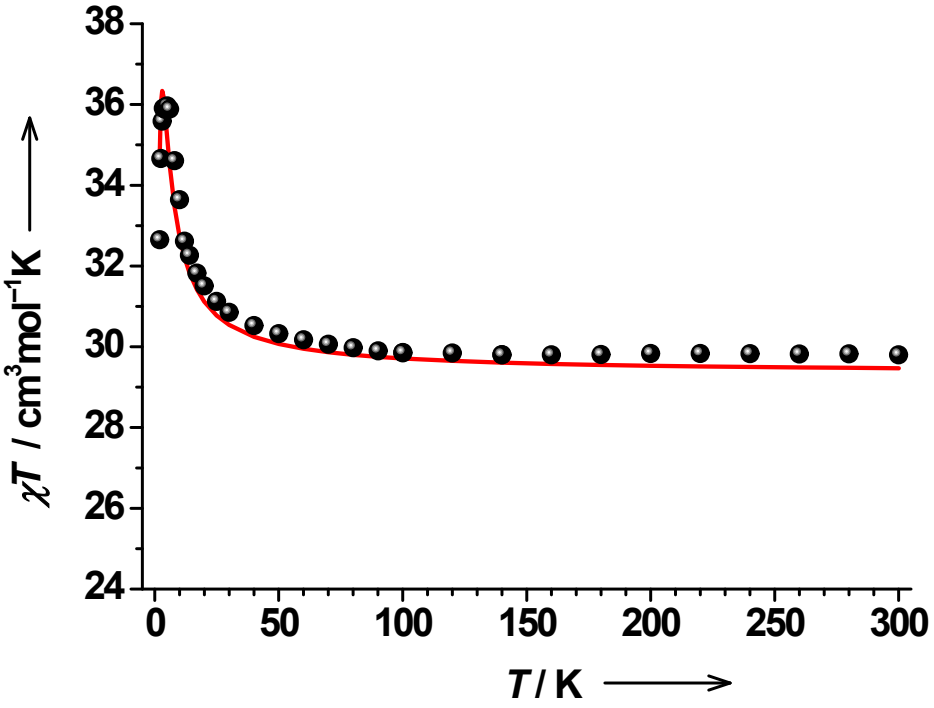

Figure S13. Temperature dependence of χT product measured on a microcrystalline sample of **2** at external magnetic field of 0.5 T. See the main text for the fit (red curve).

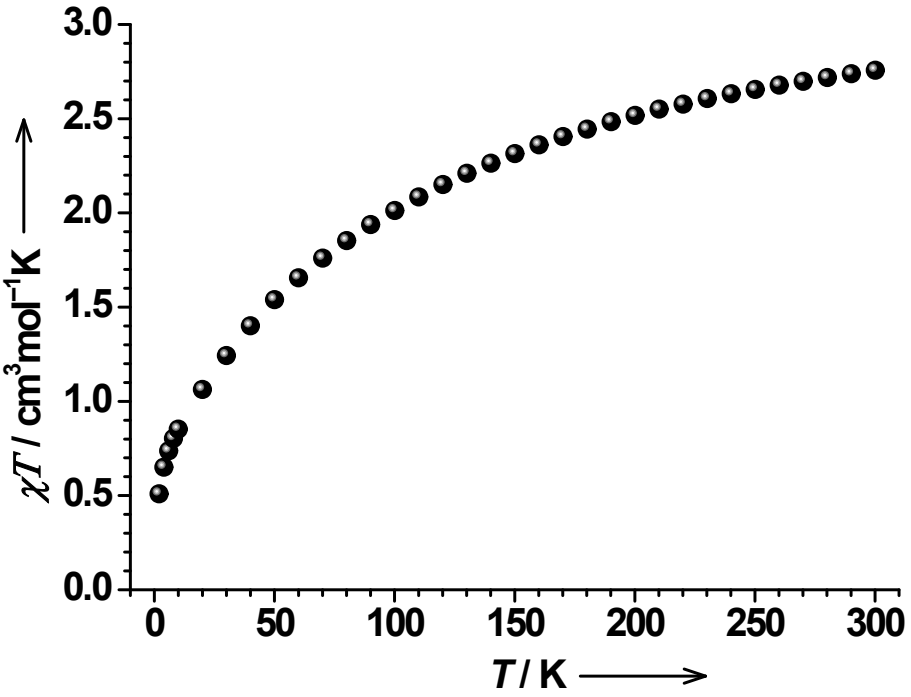

Figure S14. Temperature-dependent χT product of **3** measured at external magnetic field B = 1T.

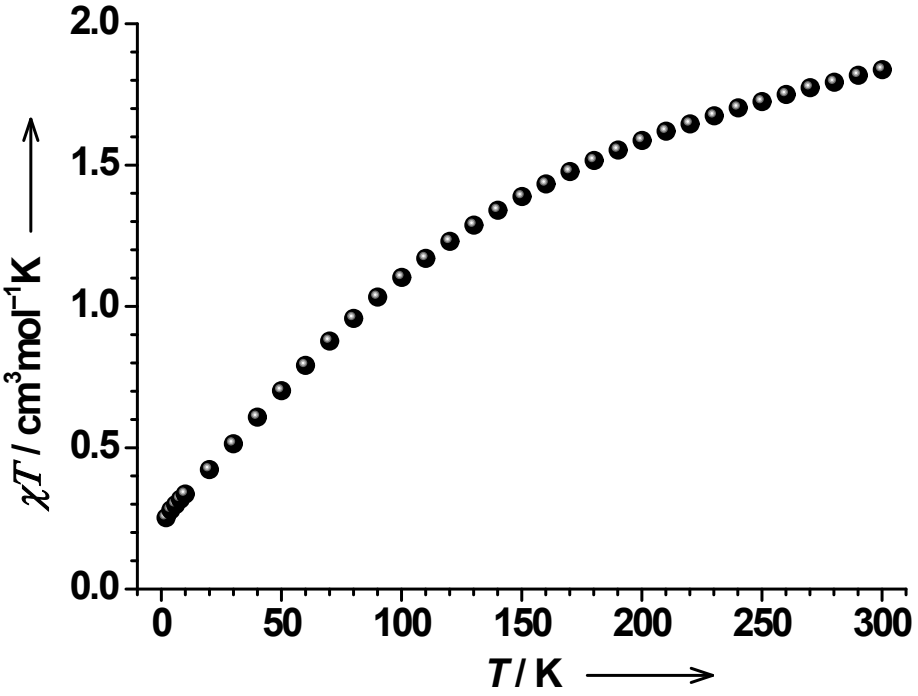

Figure S15. Temperature-dependent χT product of **4** measured at external magnetic field B = 1T.

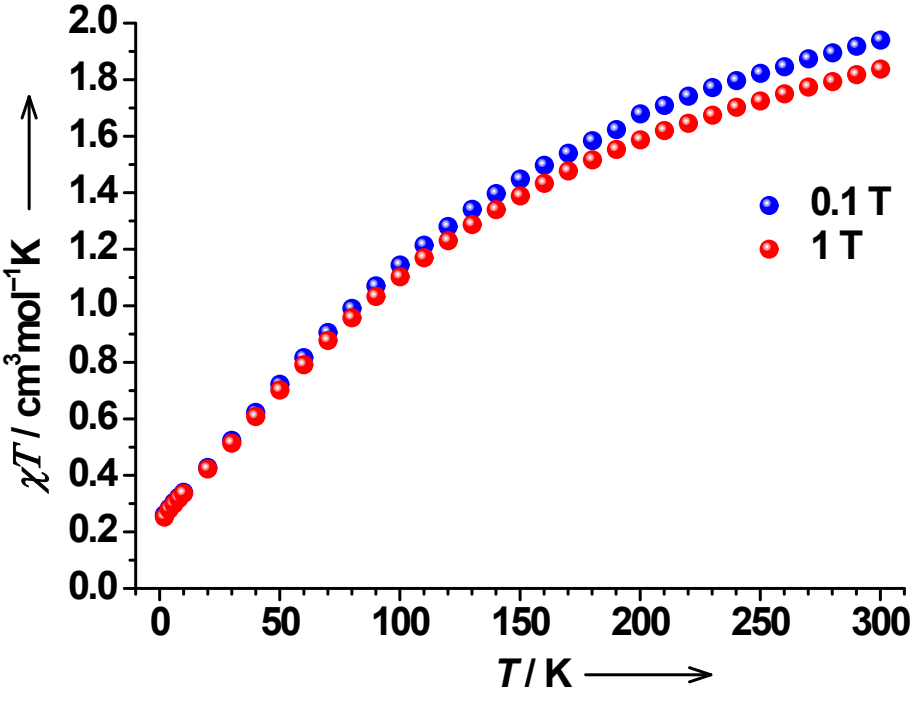

Figure S16. Temperature dependence of χT product measured on a microcrystalline sample of **4** at different magnetic fields.

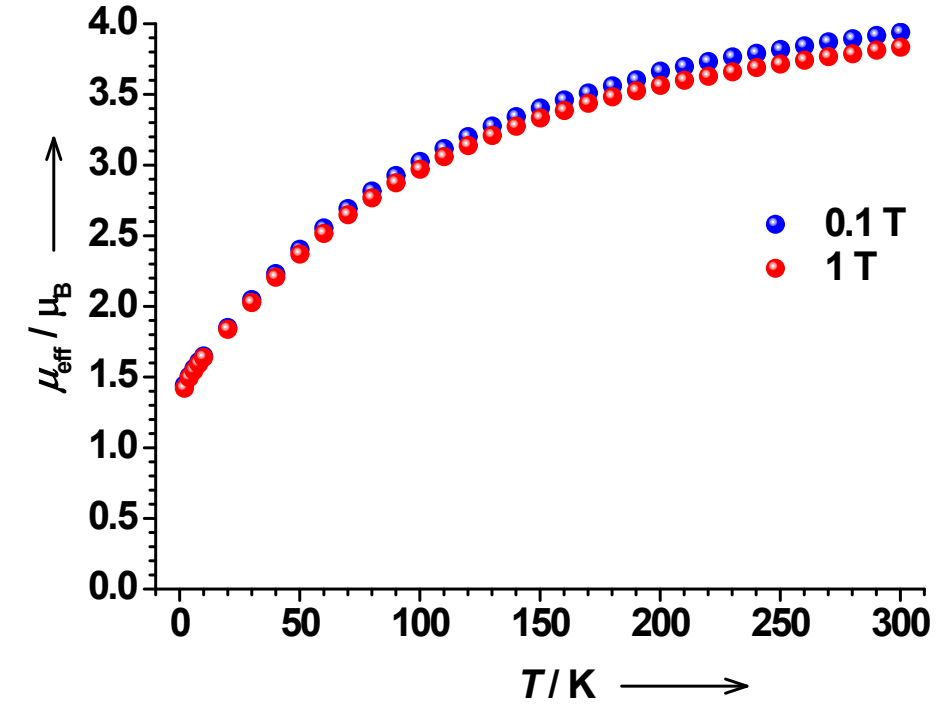

Figure S17. Temperature dependence of effective magnetic moment measured on a microcrystalline sample of **4** at different magnetic fields.

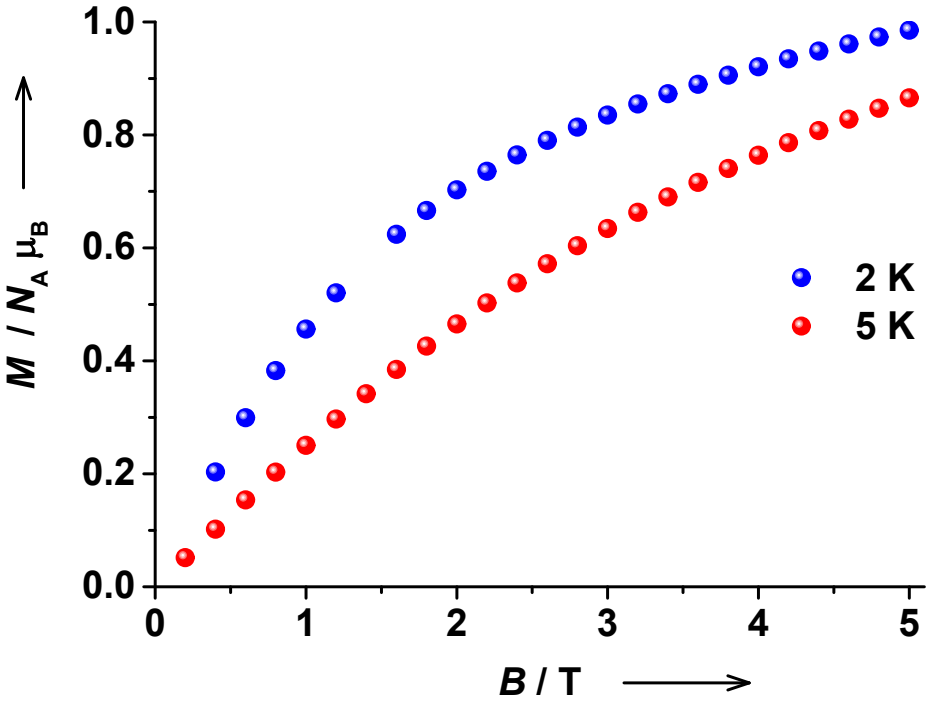

Figure S18. Field-dependent reduced magnetization measured on a microcrystalline **3** at different low temperatures.

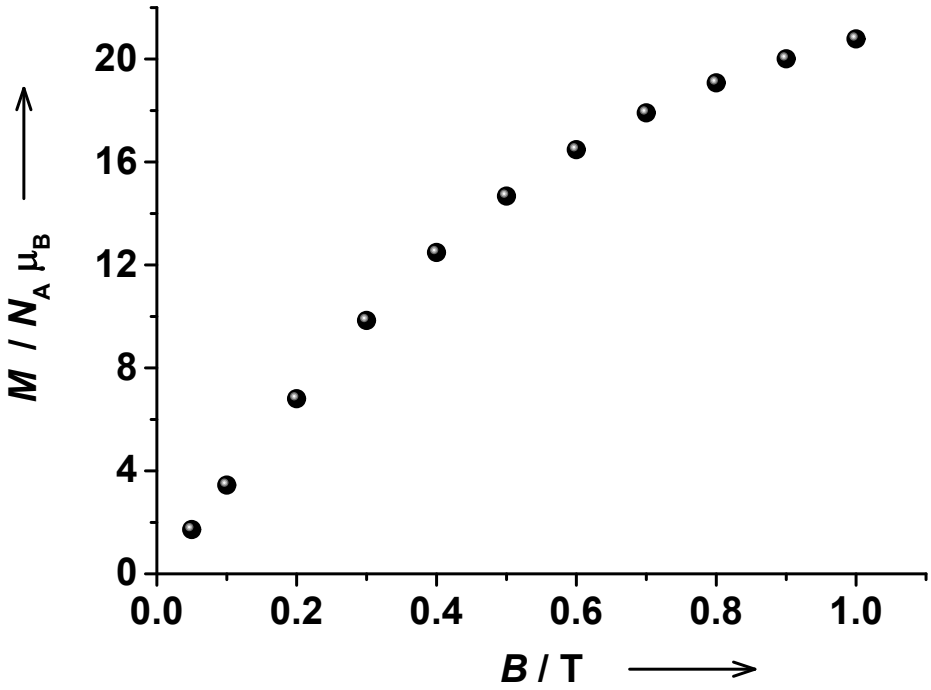

Figure S19. Field-dependent reduced magnetization measured on a microcrystalline **2** at 2 K.

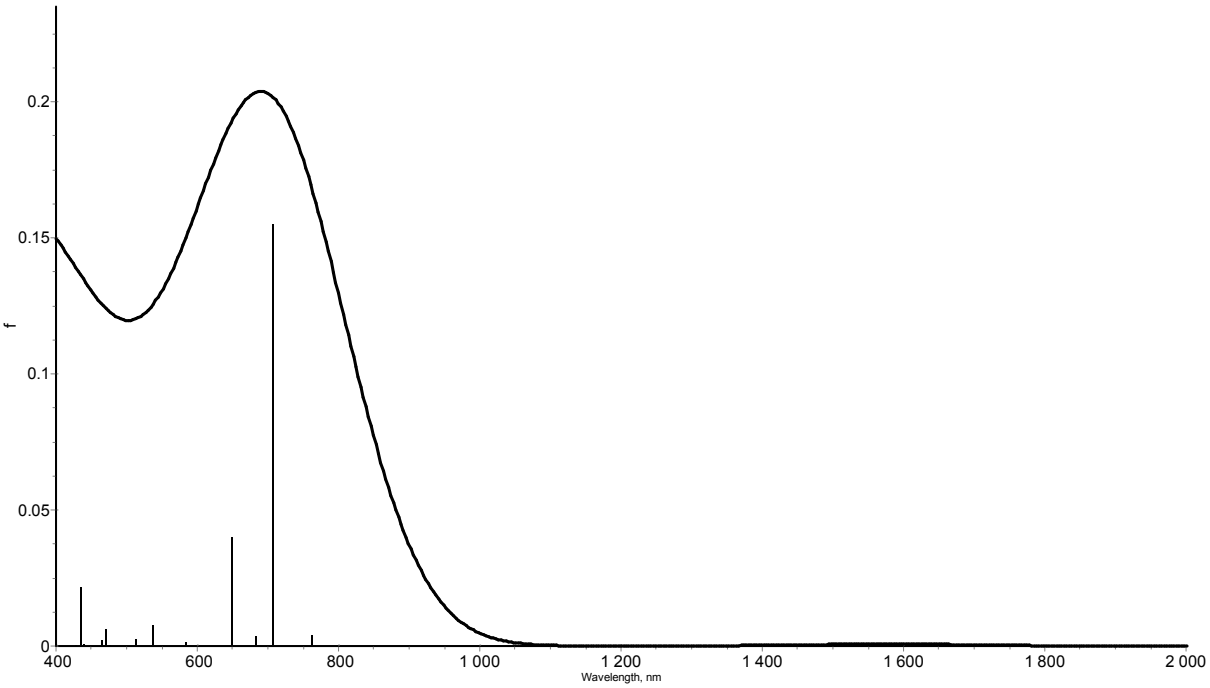

Figure S20. Calculated electronic transitions of **3** (TDA-DFT UB3LYP/def2-SVP) for gas phase.

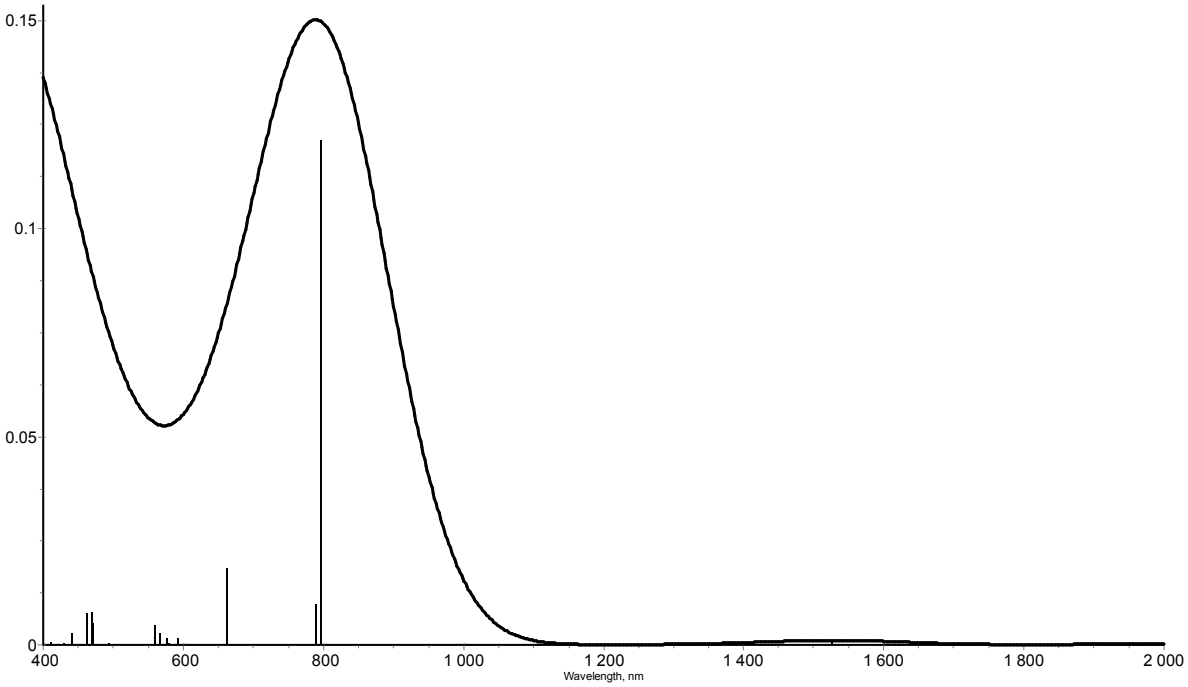

Figure S21. Calculated electronic transitions of **3** (TDA-DFT UB3LYP/def2-SVP) for solvated molecule (SMD, solvent – THF).

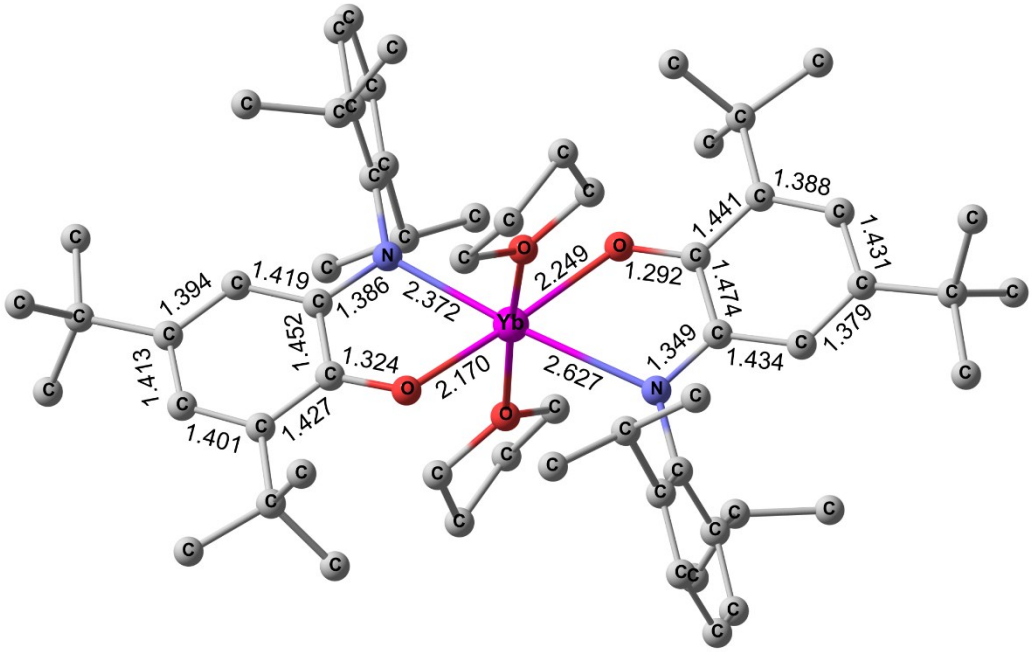

Figure S22. Optimized geometry of the compound **3-*trans*** calculated by the DFT UB3LYP/def2-SVP method. Here and in Figures S13–S15 hydrogen atoms are omitted for clarity, bond lengths are given in Å.

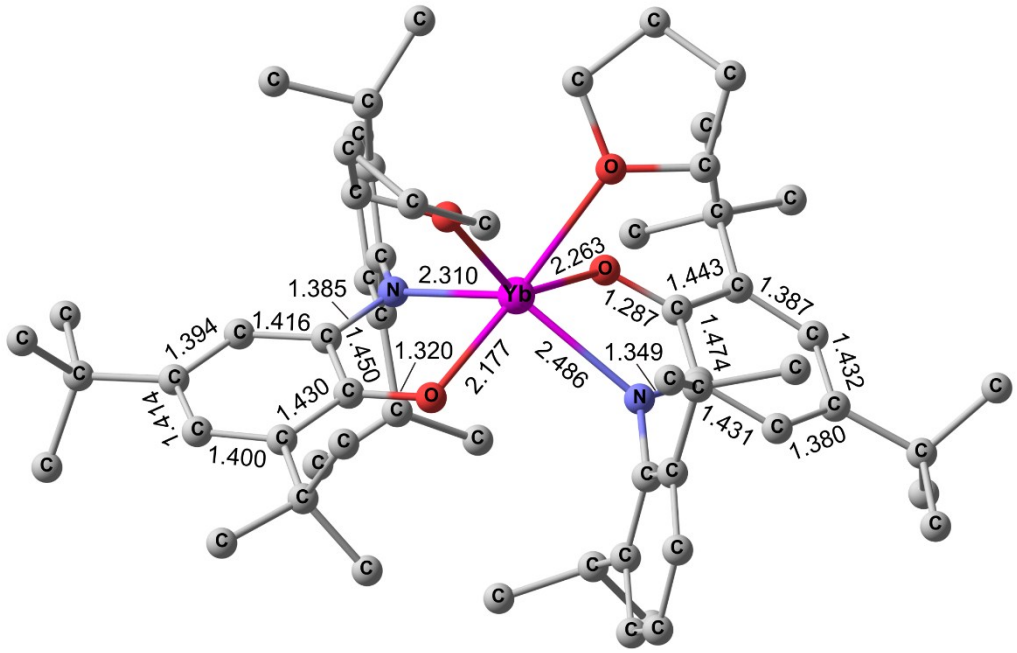

Figure S23. Optimized geometry of the compound **3-*cis*** calculated by the DFT UB3LYP/def2-SVP method.

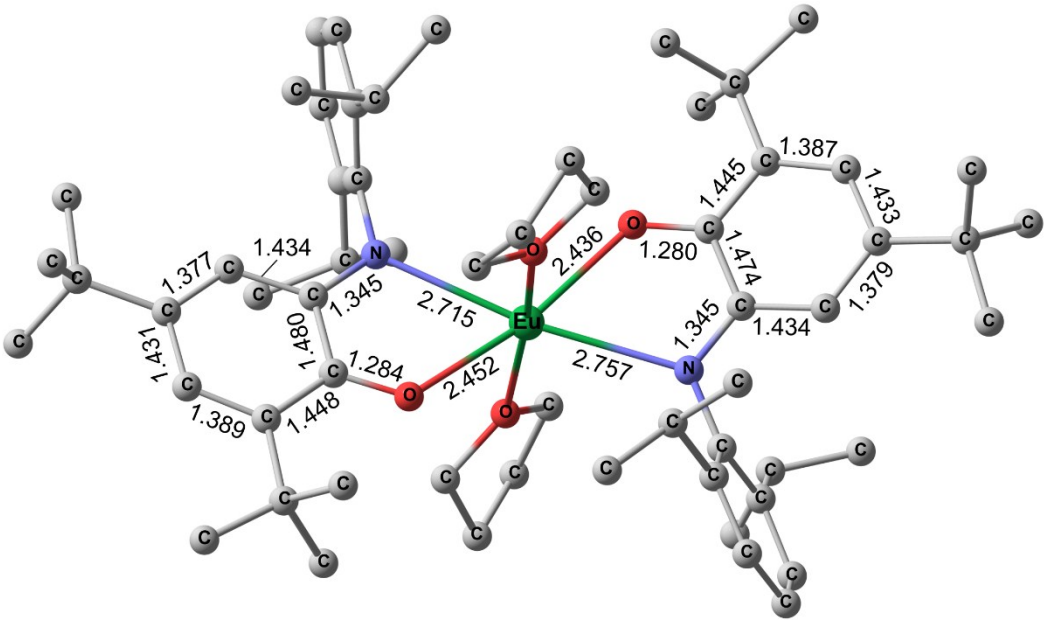

Figure S24. Optimized geometry of the compound **4-*trans*** calculated by the DFT UB3LYP/def2-SVP method.

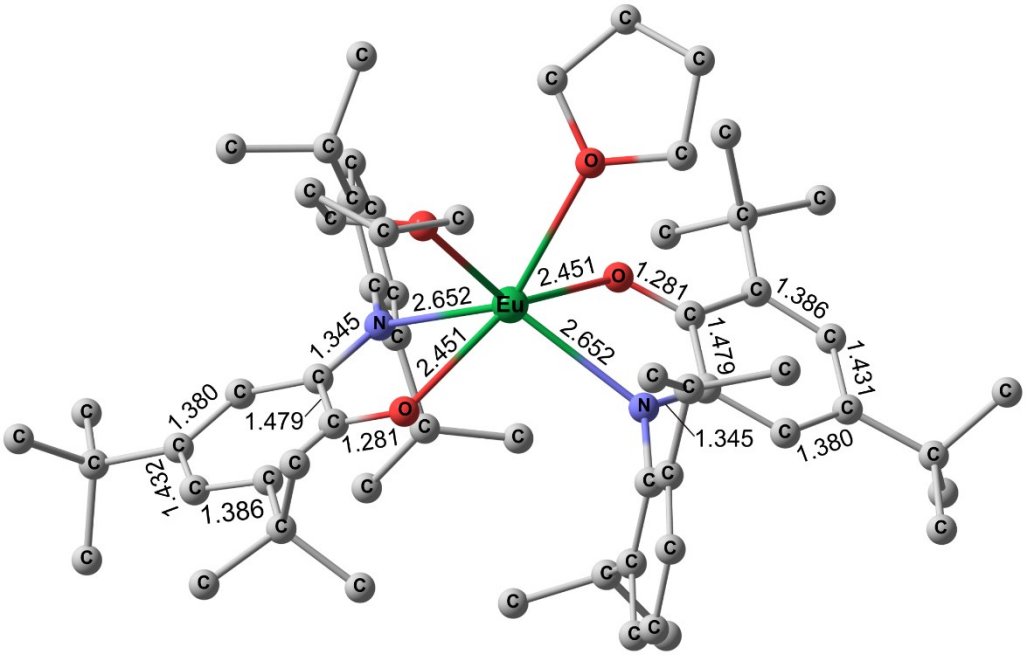

Figure S25. Optimized geometry of the compound **4-*cis*** calculated by the DFT UB3LYP/def2-SVP method.

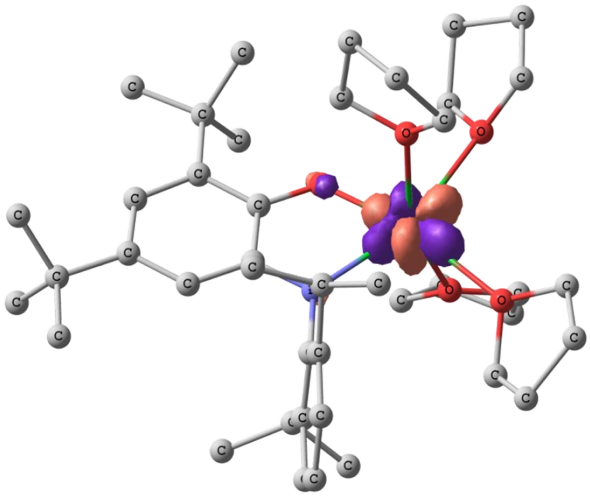

Figure S26. The HOMO of the model compound [$Yb^{II}(AP^{2-})(THF)_4$] calculated by the DFT UB3LYP/def2-SVP method. Hydrogen atoms are omitted for clarity.

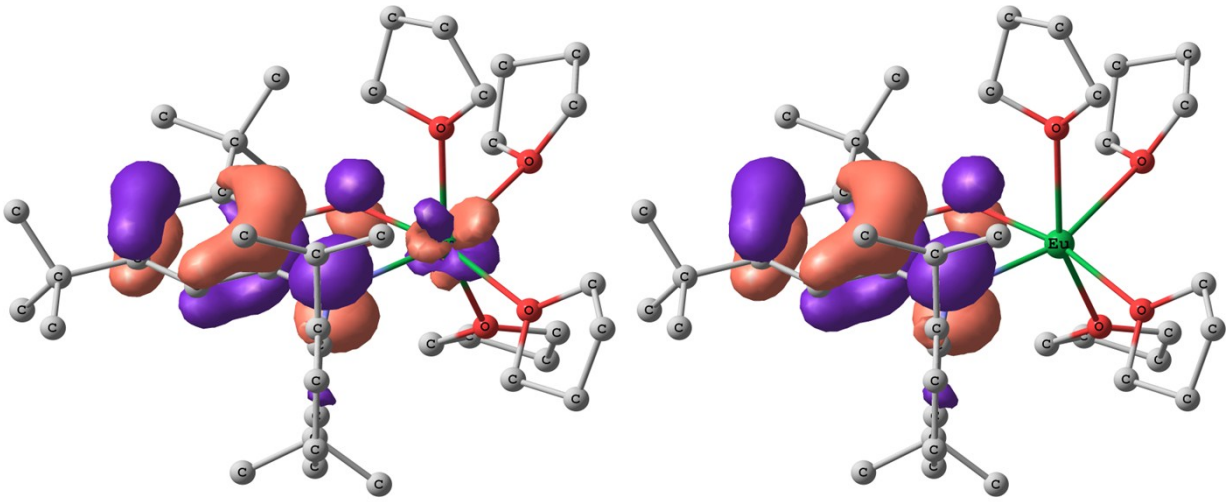

Figure S27. α-SOMO (left) and β-SOMO (right) of the model compound [$Eu^{II}(AP^{2-})(THF)_4$] calculated by the DFT UB3LYP/def2-SVP method. Hydrogen atoms are omitted for clarity.

Table S2. Spin states (S), total energies (E_{total}), relative energies (ΔE), expectation values of the spin-squared operator (S^2) and spin density at the metal center (q_s^M) of the isomers of the complexes **3** and **4** calculated by the DFT UB3LYP/def2-SVP method.

Isomer	S	E_{total}, a. u.	ΔE, kcal mol^{-1}	S^2	q_s^M
3-*trans*	2/2	-3906.53408371	0.0	2.017	0.58
3-*cis*	2/2	-3906.52839961	3.6	2.015	0.58
4-*trans*	9/2	-3457.71720551	0.0	24.778	7.04
4-*cis*	9/2	-3457.71364738	2.2	24.776	7.05

Cartesian coordinates of the isomers of the complexes 3 and 4 calculated by the DFT UB3LYP/def2-SVP method

3-*trans*

70	-0.088663000	0.071536000	0.026628000
8	-1.523878000	1.621251000	-0.472631000
8	-0.340668000	0.603255000	2.368346000
7	-2.235229000	-0.937784000	-0.006249000
6	-2.817475000	1.394307000	-0.303533000
6	-3.799736000	2.428834000	-0.350254000
6	-5.142686000	2.074677000	-0.169926000
6	-5.578197000	0.749355000	0.053619000
6	-4.613614000	-0.255687000	0.091927000
6	-3.231786000	0.022862000	-0.070425000
6	-3.394861000	3.893037000	-0.643709000
6	-7.084349000	0.468187000	0.242459000
6	0.250452000	-0.117118000	3.481427000
6	-0.611894000	0.224650000	4.696380000
6	-1.149704000	1.619211000	4.347848000
6	-1.369590000	1.518839000	2.842195000
6	-2.746108000	3.976321000	-2.045671000
6	-2.393072000	4.406726000	0.417152000
6	-4.603115000	4.850493000	-0.634229000
6	-7.376499000	-1.025426000	0.477435000
6	-7.611444000	1.256002000	1.465164000
6	-7.859023000	0.912653000	-1.021005000
1	-5.897374000	2.858118000	-0.211075000
1	-4.902329000	-1.292110000	0.255842000
1	-3.457619000	3.653982000	-2.823740000
1	-1.858099000	3.333370000	-2.099009000
1	-2.441874000	5.012880000	-2.272569000
1	-2.110671000	5.452407000	0.205924000
1	-1.480926000	3.796207000	0.421277000
1	-2.843485000	4.379783000	1.423682000
1	-5.346751000	4.591052000	-1.404136000
1	-4.259176000	5.876764000	-0.842567000

1	-5.113207000	4.865030000	0.342280000
1	-8.460359000	-1.179811000	0.605658000
1	-6.878621000	-1.404029000	1.383902000
1	-7.051332000	-1.647010000	-0.371488000
1	-7.471852000	2.341460000	1.345562000
1	-7.085832000	0.951104000	2.384820000
1	-8.689658000	1.071939000	1.612160000
1	-7.512062000	0.359698000	-1.908949000
1	-7.729445000	1.986576000	-1.225555000
1	-8.939760000	0.723019000	-0.902294000
1	1.285792000	0.228747000	3.604799000
1	0.266901000	-1.188118000	3.237794000
1	-0.033344000	0.201554000	5.632017000
1	-1.442720000	-0.491141000	4.795477000
1	-2.076726000	1.871829000	4.883702000
1	-0.402558000	2.394560000	4.581383000
1	-1.254265000	2.468466000	2.305473000
1	-2.355476000	1.094876000	2.591888000
8	1.420213000	-1.577241000	0.278596000
8	0.320223000	-0.138829000	-2.377445000
7	2.381699000	0.949690000	0.192844000
6	2.696905000	-1.438300000	0.140166000
6	3.596984000	-2.561398000	0.065974000
6	4.945399000	-2.301474000	-0.138411000
6	5.506756000	-0.991897000	-0.267696000
6	4.659685000	0.089573000	-0.146287000
6	3.251261000	-0.074394000	0.066969000
6	3.064173000	-4.003077000	0.224000000
6	7.018139000	-0.851128000	-0.533720000
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1	6.892423000	-2.782952000	-2.393841000
1	6.490097000	-1.253586000	-3.213859000
1	8.194713000	-1.666716000	-2.880655000
1	8.038442000	-1.102509000	0.856013000
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1	9.099838000	-1.579398000	-0.500494000
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1	0.680240000	1.167809000	-4.786902000
1	1.584667000	-1.099631000	-5.148242000
1	0.027535000	-1.837839000	-4.706752000
1	1.078103000	-1.978270000	-2.536525000
1	2.091865000	-0.532394000	-2.843778000

6	-2.843591000	-2.228898000	0.568123000
6	-2.894148000	-3.175913000	-0.495211000
6	-3.258451000	-4.499095000	-0.203604000
1	-3.304222000	-5.232972000	-1.014422000
6	-3.555962000	-4.904485000	1.097127000
1	-3.844358000	-5.940691000	1.302618000
6	-3.477203000	-3.978419000	2.135882000
1	-3.707389000	-4.302417000	3.155667000
6	-3.117051000	-2.642893000	1.901352000
6	-2.550503000	-2.786203000	-1.935304000
1	-2.041918000	-1.812583000	-1.890303000
6	-1.587954000	-3.783682000	-2.599634000
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1	-2.475655000	-0.785869000	2.717453000
6	-4.454412000	-1.153700000	3.473041000
1	-4.967268000	-0.671499000	2.625062000
1	-4.390319000	-0.417872000	4.295233000
1	-5.087566000	-1.987947000	3.824875000
6	-2.313434000	-2.242292000	4.289395000
1	-1.327692000	-2.652057000	4.009740000
1	-2.884711000	-3.054904000	4.770380000
1	-2.156292000	-1.464702000	5.056180000
6	3.237248000	2.231910000	0.302970000
6	3.875237000	2.684641000	1.494544000
6	4.428904000	3.973128000	1.514811000
1	4.932703000	4.324765000	2.421451000
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1	4.830717000	5.804740000	0.433101000

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6	3.985906000	1.799371000	2.738739000
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6	5.433507000	1.328135000	2.994290000
1	5.835689000	0.780681000	2.127506000
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6	3.421932000	2.486514000	3.997568000
1	2.392977000	2.851136000	3.835734000
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1	3.409805000	1.780738000	4.846997000
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1	4.142116000	3.141571000	-3.465692000
1	3.044972000	1.891683000	-4.109964000

4-*cis*

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1	3.235272000	-0.984648000	-2.565777000
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1	4.109431000	-1.745584000	-4.702487000
1	3.049291000	-0.642420000	-5.614184000

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1	-2.021601000	-6.313879000	1.445036000
6	-1.740781000	-4.295278000	2.168842000
1	-1.487487000	-4.625323000	3.180071000
6	-1.754595000	-2.922584000	1.883017000
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6	-2.150054000	-3.967529000	-2.946146000
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1	-7.820595000	1.192851000	1.136735000
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1	-4.506307000	-2.550510000	-3.044880000
7	-2.045997000	-1.128215000	0.216051000
6	-3.044540000	-0.308340000	0.590070000
1	-2.288313000	-2.043430000	-2.007948000
1	-2.309259000	-3.529744000	-3.945927000
6	-2.849140000	1.136437000	0.340625000
1	-2.637381000	3.312241000	-1.409283000
1	-1.621741000	3.612605000	0.963707000
8	-1.745684000	1.528933000	-0.177343000
1	-1.498186000	-0.918398000	2.580270000
6	6.676967000	1.707165000	2.415007000
1	4.373742000	1.737904000	1.435981000
1	7.644981000	1.958158000	2.877987000
1	5.884696000	2.040868000	3.103066000
1	6.590462000	2.294636000	1.487427000
6	2.080913000	2.462729000	0.682415000
6	2.373270000	3.482736000	-0.266141000
6	2.362188000	4.822259000	0.146749000
1	2.598341000	5.609659000	-0.573109000
6	2.059215000	5.172734000	1.461676000
1	2.055709000	6.222703000	1.766323000
6	1.751453000	4.171488000	2.380816000
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6	1.752213000	2.815920000	2.022084000
6	2.738610000	3.128246000	-1.705238000
6	2.152102000	4.098926000	-2.742988000
1	1.070490000	4.248375000	-2.594409000
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6	4.263626000	2.997788000	-1.885365000
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6	4.261201000	0.679190000	1.209466000
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6	6.603717000	0.193445000	2.144511000
6	3.501365000	-3.791101000	-1.257849000
6	2.538566000	-4.173985000	1.046010000
6	4.987296000	-4.412220000	0.642282000
6	6.768219000	-0.545679000	3.494214000
6	7.777236000	-0.183690000	1.209003000
1	5.859683000	-2.293156000	1.397476000
1	4.364331000	-3.423739000	-1.839105000
1	3.371623000	-4.861944000	-1.490260000
1	2.418536000	-5.248108000	0.823630000
1	2.699617000	-4.070957000	2.131460000
1	5.886633000	-4.080435000	0.098423000
1	4.822511000	-5.472298000	0.390732000
1	5.200896000	-4.361560000	1.721862000
1	6.765755000	-1.639553000	3.369232000
1	5.951209000	-0.286523000	4.186653000
1	7.722363000	-0.267775000	3.973276000
1	7.692287000	0.337016000	0.241352000
1	7.813786000	-1.265019000	1.005582000
1	8.740519000	0.101024000	1.665072000
1	4.518692000	2.703828000	-2.918573000
7	2.037088000	1.108433000	0.266323000
6	3.036427000	0.268396000	0.590009000

1	2.308098000	2.131779000	-1.901515000
1	2.312299000	3.713825000	-3.764104000
6	2.834902000	-1.161727000	0.270937000
1	2.601115000	-3.252143000	-1.580177000
1	1.604619000	-3.660741000	0.785065000
8	1.725514000	-1.525440000	-0.255174000
1	1.447594000	0.781574000	2.599958000

Table S3. Crystallographic data and refinement details

	1·0.6C_6H_{14}	**2**·0.5C_6H_{14}	**3-*dimer***·C_7H_8
Chemical formula	$C_{115.60}H_{172.40}N_4O_6Yb_4$	$C_{115}H_{171}Eu_4N_4O_6$	$C_{111}H_{156}N_4O_4Yb_2$
M_r	2406.32	2313.39	1956.47
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Temperature (K)	150	100	150
a, *b*, *c* (Å)	13.0617 (5), 13.9854 (6), 17.7771 (7)	13.0158 (16), 13.8449 (17), 17.793 (2)	26.4227(16), 13.2020(6), 31.9679(16)
α, β, γ (°)	103.9973 (14), 95.5535 (13), 114.9932 (13)	103.499 (2), 95.709 (2), 114.532 (2)	90 114.589(4) 90
V (Å^3)	2781.9 (2)	2765.6 (6)	10140.2(10)
Z	1	1	4
Radiation type	Mo *Kα*	Mo *Kα*	Mo *Kα*
μ (mm^{-1})	3.38	2.29	1.89
Crystal size (mm)	0.20 × 0.05 × 0.05	0.25 × 0.21 × 0.04	0.22 × 0.16 × 0.10
Diffractometer	Bruker Apex Duo	Bruker Apex Duo	Bruker Apex Duo
Absorption correction	Multi-scan *SADABS* (Bruker-AXS, 2004)	Multi-scan *SADABS* (Bruker-AXS, 2004)	Multi-scan *SADABS* (Bruker-AXS, 2004)
T_{min}, T_{max}	0.563, 0.723	0.571, 0.757	0.688, 0.829
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	49834, 11128, 8584	28195, 14032, 9290	64240, 23529, 18138
R_{int}	0.044	0.048	0.057
θ values (°)	θ_{max} = 26.2, θ_{min} = 1.7	θ_{max} = 28.6, θ_{min} = 2.4	θ_{max} = 27.6, θ_{min} = 1.7
Range of *h*, *k*, *l*	-16 ≤ *h* ≤ 16, -17 ≤ *k* ≤ 17, -21 ≤ *l* ≤ 21	-17 ≤ *h* ≤ 17, -18 ≤ *k* ≤ 18, -23 ≤ *l* ≤ 23	-34 ≤ *h* ≤ 34, -11 ≤ *k* ≤ 17, -28 ≤ *l* ≤ 41
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.035, 0.091, 1.03	0.050, 0.117, 1.02	0.038, 0.085, 1.07
No. of reflections, parameters, restraints	11128, 594, 18	14032, 596, 0	23529, 1131, 65
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 8.8153P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 13.880P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[s^2(F_o^2) + (0.0430P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.98, -1.49	1.72, -2.66	2.31, -1.00

Computer programs: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

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