Supplementary information

On the usability of salt metathesis reactions for the synthesis of sterically crowded *tris*-formamidinate Ln(III) complexes: success and limits. Spontaneous reduction of Eu(III) to Eu(II).

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Table of contents:

1. X-ray structural determination

Table S1. Crystal data and structure refinement for **1**–**5**.

Identification code	**1Eu**	**2Eu**·2.5C_7H_8	**3Eu**	**1Nd**·2THF	**2Nd**
Empirical formula	$C_{54}H_{78}ClEuN_4O$	$C_{92.5}H_{125}EuN_6$	$C_{58}H_{86}EuN_4O_2$	$C_{66}H_{102}ClN_4NdO_4$	$C_{75}H_{105}N_6Nd$
Formula weight	986.61	1472.94	1023.26	1195.20	1234.88
Temperature/K	298(2)	150(2)	150(2)	150(4)	150(2)
Space group	*P*–1	$P2_1/n$	*P*–1	$P2_1/n$	$P2_1/n$
a/Å	11.367(5)	13.1230(3)	12.0671(7)	10.7849(5)	13.0830(3)
b/Å	14.758(5)	37.9400(7)	12.7845(8)	27.0152(13)	20.4856(5)
c/Å	16.373(6)	16.4938(3)	19.7004(12)	21.9212(10)	26.3710(6)
α/°	84.017(11)	90	84.194(2)	90	90
β/°	78.118(12)	96.3750(10)	86.763(2)	94.8470(10)	100.0750(10)
γ/°	80.397(11)	90	64.066(2)	90	90
Volume/Å^3	2643.2(17)	8161.3(3)	2718.9(3)	6364.0(5)	6958.8(3)
Z	2	4	2	4	4
ρ_{calc}g/cm^3	1.240	1.199	1.250	1.247	1.179
μ/mm^{-1}	1.276	5.854	1.196	0.906	0.790
F(000)	1036.0	3140.0	1082.0	2540.0	2628.0
Crystal size/mm^3	0.27 × 0.17 × 0.08	0.35 × 0.17 × 0.1	0.26 × 0.14 × 0.1	0.15 × 0.1 × 0.08	0.13 × 0.08 × 0.08
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.702 to 48.806	4.658 to 127.9	3.556 to 51.656	4.022 to 52.838	3.274 to 61.068
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -19 ≤ l ≤ 16	-14 ≤ h ≤ 15, -44 ≤ k ≤ 44, -18 ≤ l ≤ 19	-14 ≤ h ≤ 14, -15 ≤ k ≤ 13, -24 ≤ l ≤ 23	-13 ≤ h ≤ 13, -31 ≤ k ≤ 33, -27 ≤ l ≤ 27	-18 ≤ h ≤ 18, -29 ≤ k ≤ 29, -37 ≤ l ≤ 37
Reflections collected	22217	64727	22668	70871	139058
Independent reflections	8545 [R_{int} = 0.1694, R_{sigma} = 0.2763]	13430 [R_{int} = 0.0655, R_{sigma} = 0.0523]	10342 [R_{int} = 0.0429, R_{sigma} = 0.0762]	13055 [Rint = 0.0700, Rsigma = 0.0515]	21263 [Rint = 0.0627, Rsigma = 0.0465]
Data/restraints/parameters	8545/0/566	13430/85/821	10342/33/621	13055/2/651	21263/0/739
Goodness-of-fit on F^2	0.944	1.135	1.017	1.103	1.301
Final R indexes [I>=2σ (I)]	R_1 = 0.0677, wR_2 = 0.0852	R_1 = 0.0586, wR_2 = 0.1367	R_1 = 0.0402, wR_2 = 0.0687	R1 = 0.0590, wR2 = 0.1287	R1 = 0.0763, wR2 = 0.1403
Final R indexes [all data]	R_1 = 0.1985, wR_2 = 0.1113	R_1 = 0.0672, wR_2 = 0.1409	R_1 = 0.0578, wR_2 = 0.0737	R1 = 0.0735, wR2 = 0.1354	R1 = 0.1073, wR2 = 0.1490
rgest diff. peak/hole / e Å^{-3}	1.49/-2.03	1.01/-0.78	0.54/-0.49	0.94/-2.00	1.08/-1.09

2. Powder X-ray studies

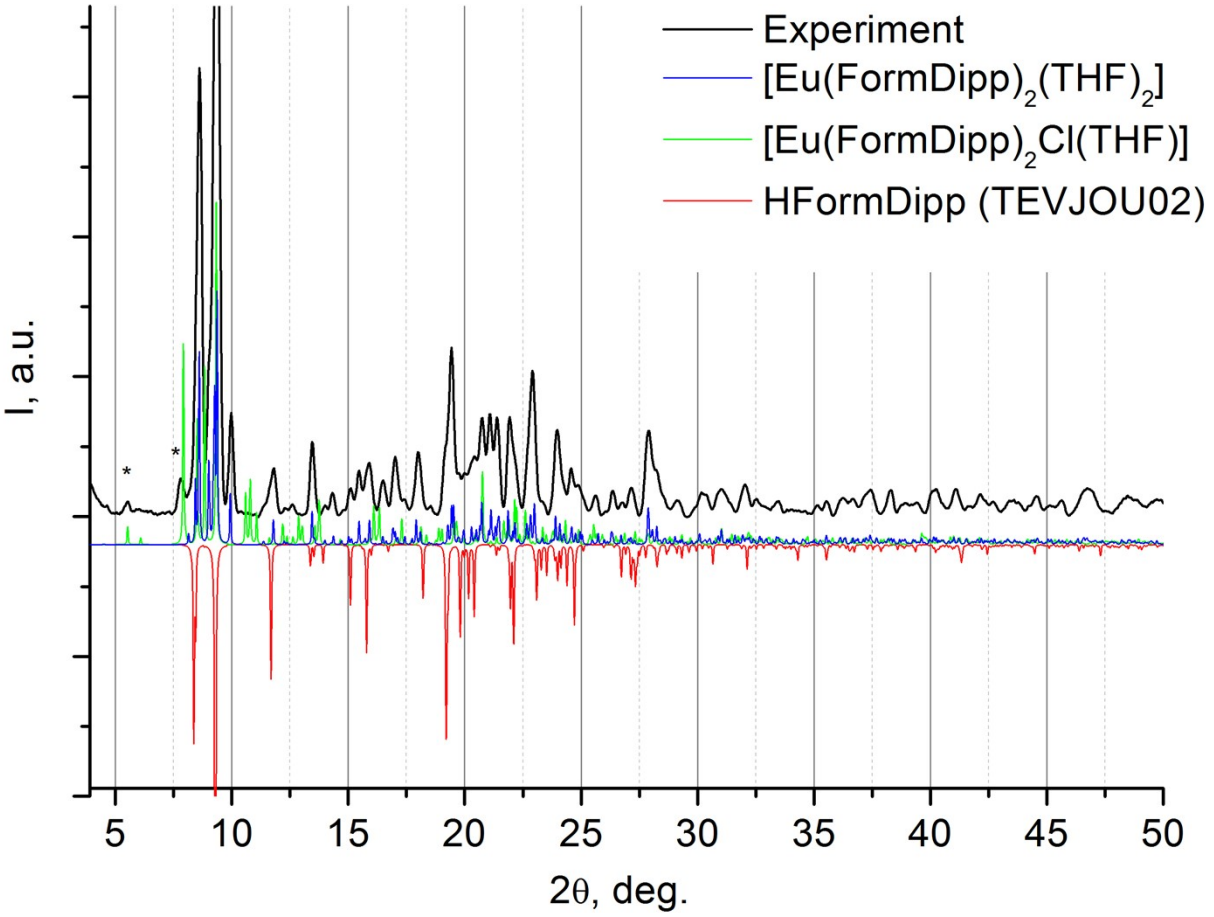

Figure S1. PXRD pattern (black) of the reaction mixture of $EuCl_3$ and KFormDipp in a molar ratio of 1 : 3 in THF after removal of volatiles, measured at 150K (Cu Kα radiation). Simulated PXRD patterns of the compounds (coloured). $[Eu(FormDipp)_2(THF)_2]$ is the major phase, $[Eu(FormDipp)_2Cl(THF)]$ is the minor phase (peaks assigned to the latter are marked with "*"). No phases of HFormDipp were detected, but one of the polymorphs (CCDC Refcode TEVJOU02) can present as an admixture, since its peaks are hidden by those of the major phase.

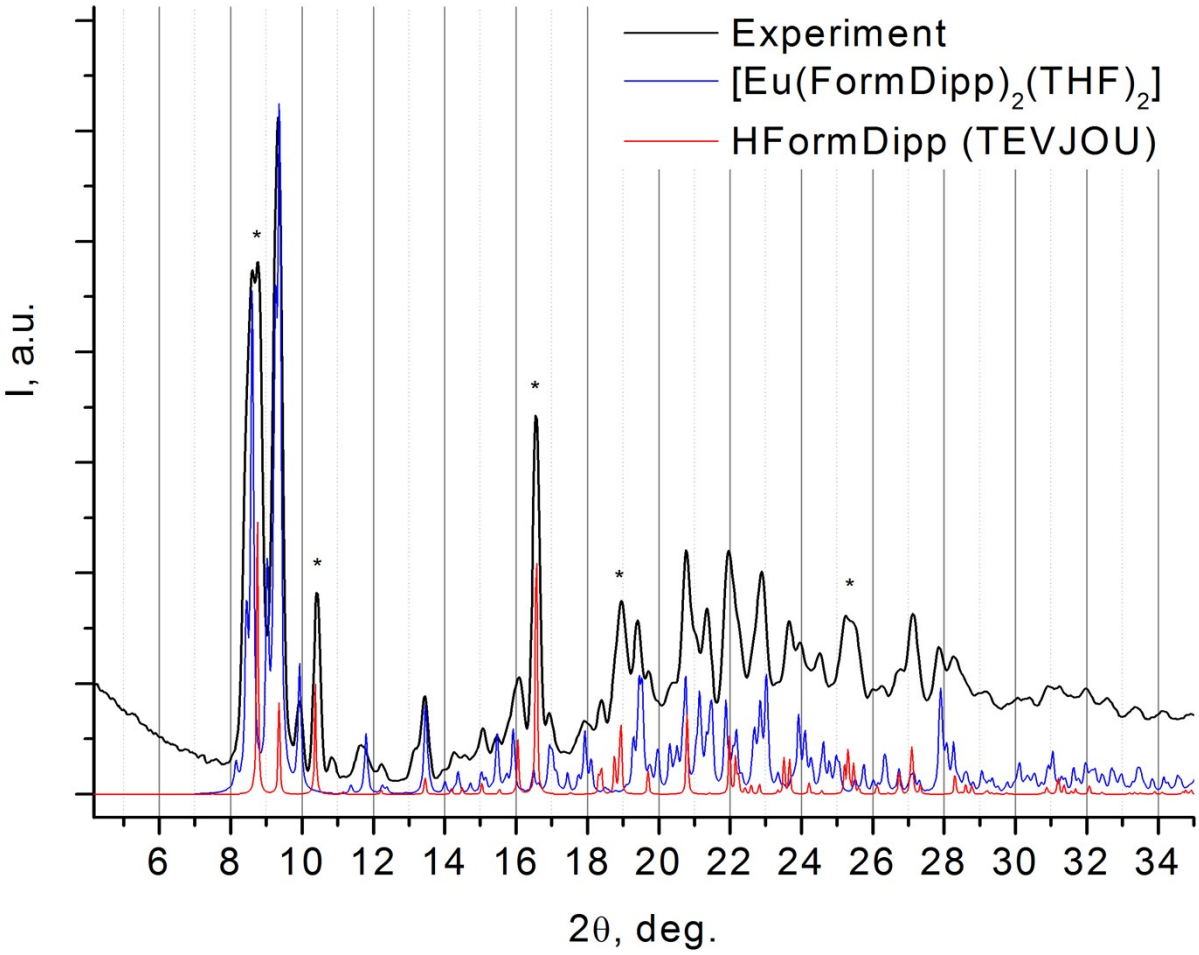

Figure S2. PXRD pattern (black) of sample **3Eu** at 150 K (Cu Kα radiation). Simulated PXRD patterns of $[Eu(FormDipp)_2(THF)_2]$ (blue) and HFormDipp (red; CCDC Refcode TEVJOU). Peaks assigned to the latter are marked with "*".

3. Additional information

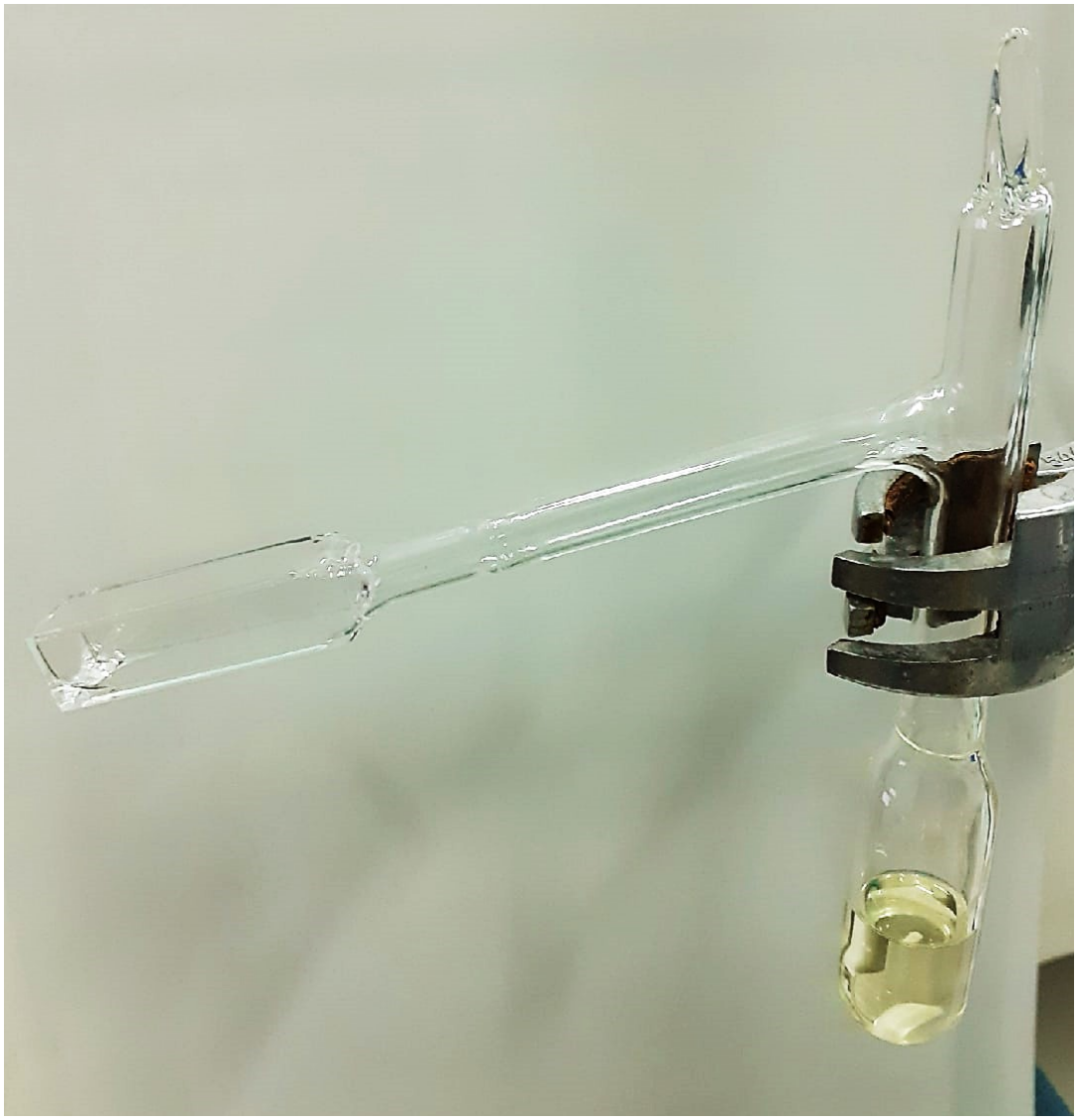

Figure S3. The photo of an ampoule equipped with a cuvette for the absorption studies.

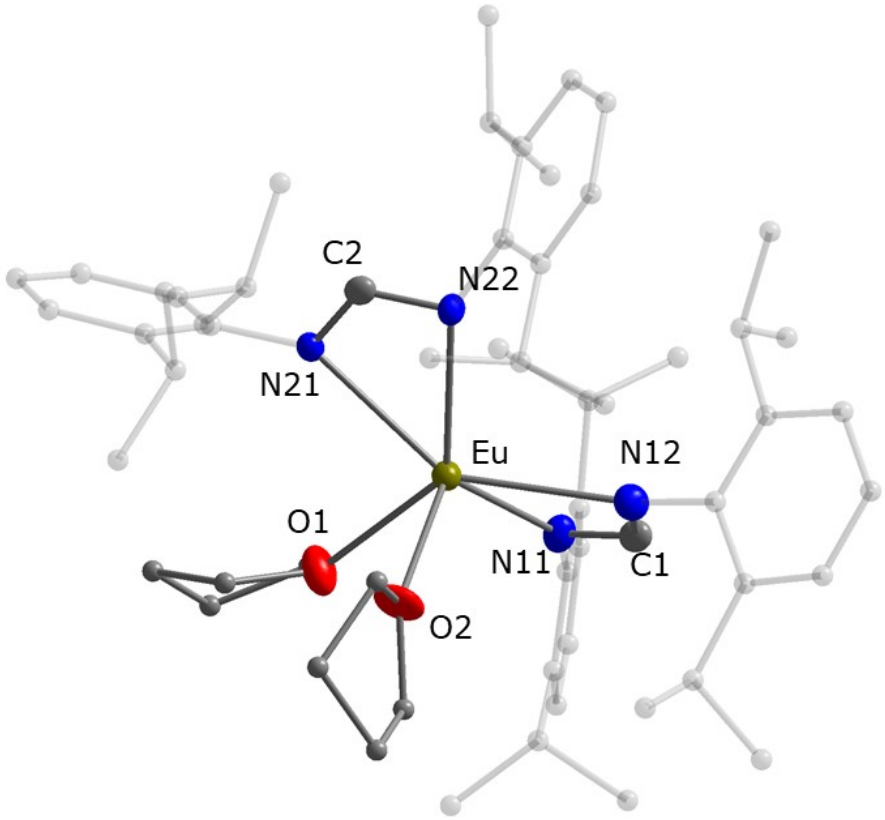

Figure S4. Molecular structure of the complex **3Eu**. Disordered atoms and hydrogens omitted for clarity; Dipp substituents are faded. Atomic displacement ellipsoids are drawn at the 50% probability level.

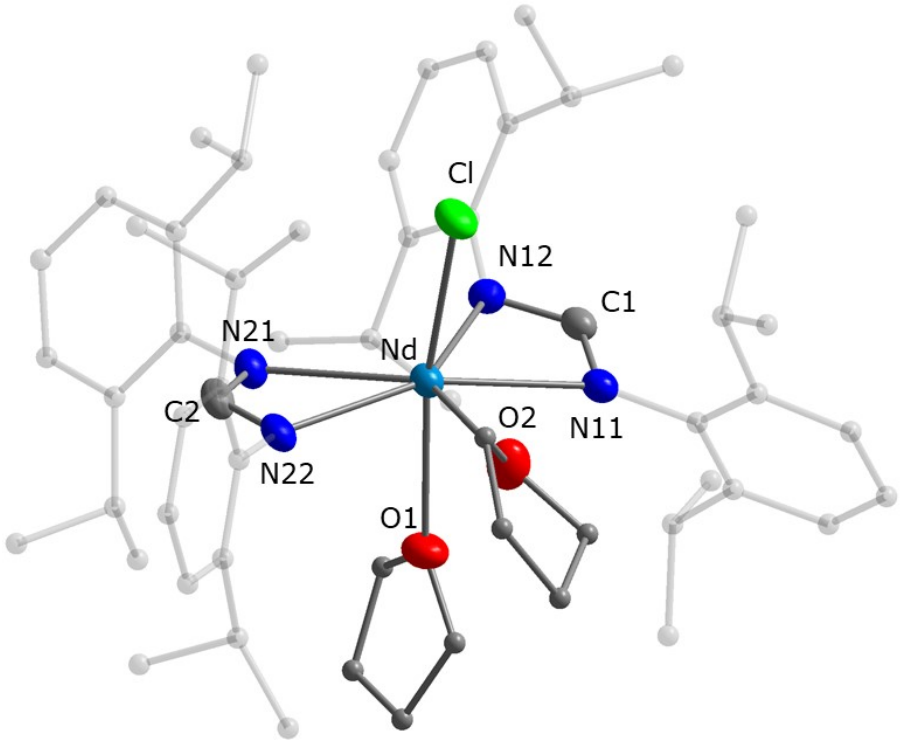

Figure S5. Molecular structure of the complex **1Nd**. Disordered atoms and hydrogens omitted for clarity; Dipp substituents are faded. Atomic displacement ellipsoids are drawn at the 50% probability level.

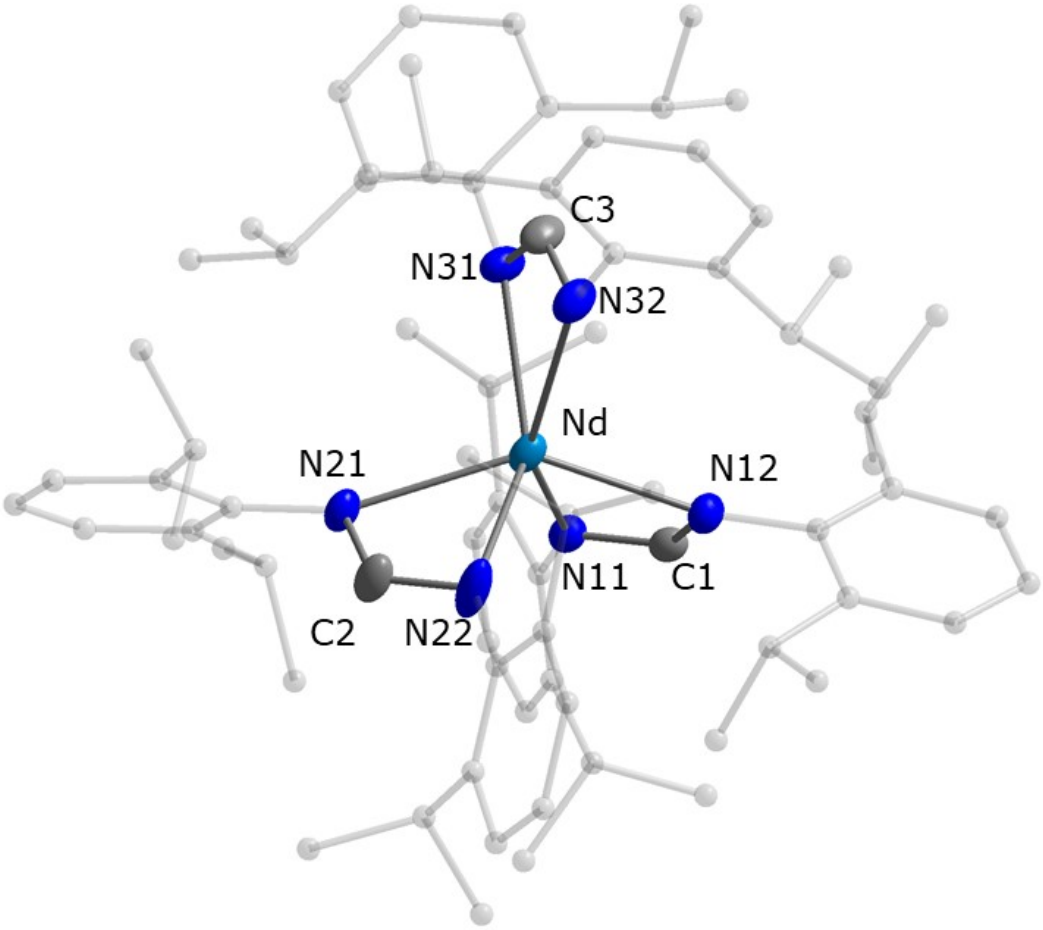

Figure S6. Molecular structure of the complex **2Nd**. Disordered atoms and hydrogens omitted for clarity; Dipp substituents are faded. Atomic displacement ellipsoids are drawn at the 50% probability level.

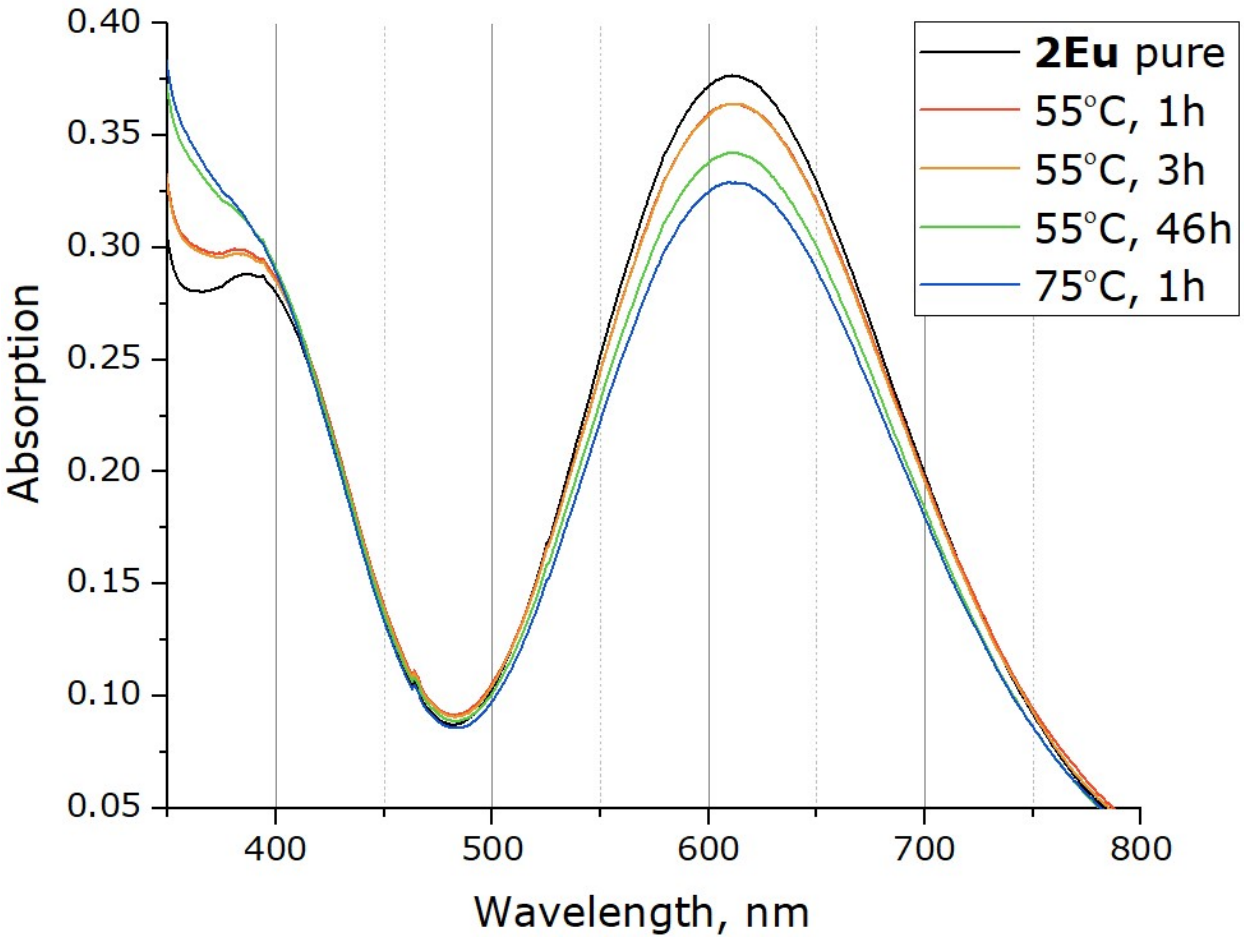

Figure S7. Differences in absorption in kinetic studies conducted at 55°C versus 75°C, measured for 10^{-3} M **2Eu** solution in thf in the sealed 10-mm quartz cuvette.

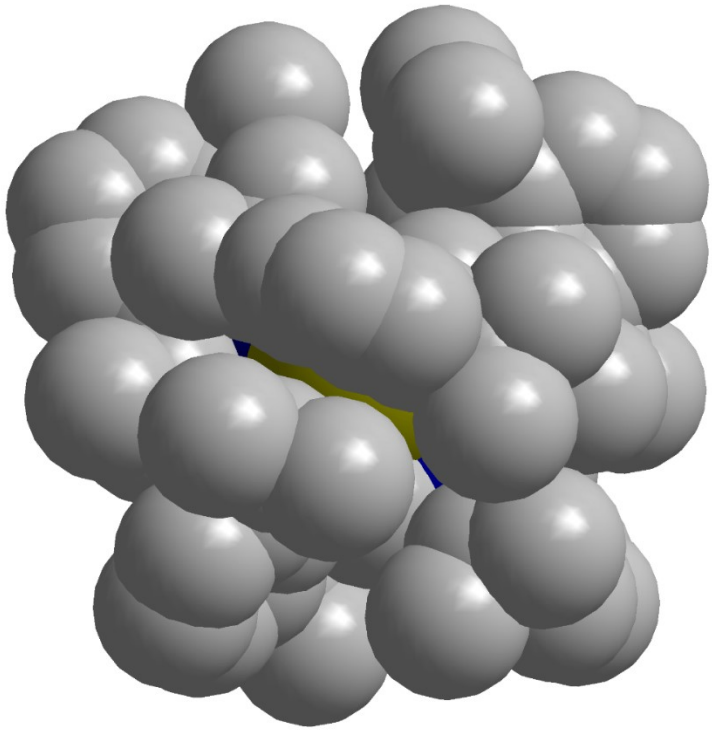

Figure S8. Molecular structure of **2Eu** shown in van der Waals spheres. Hydrogens omitted for clarity.