Supplementary information

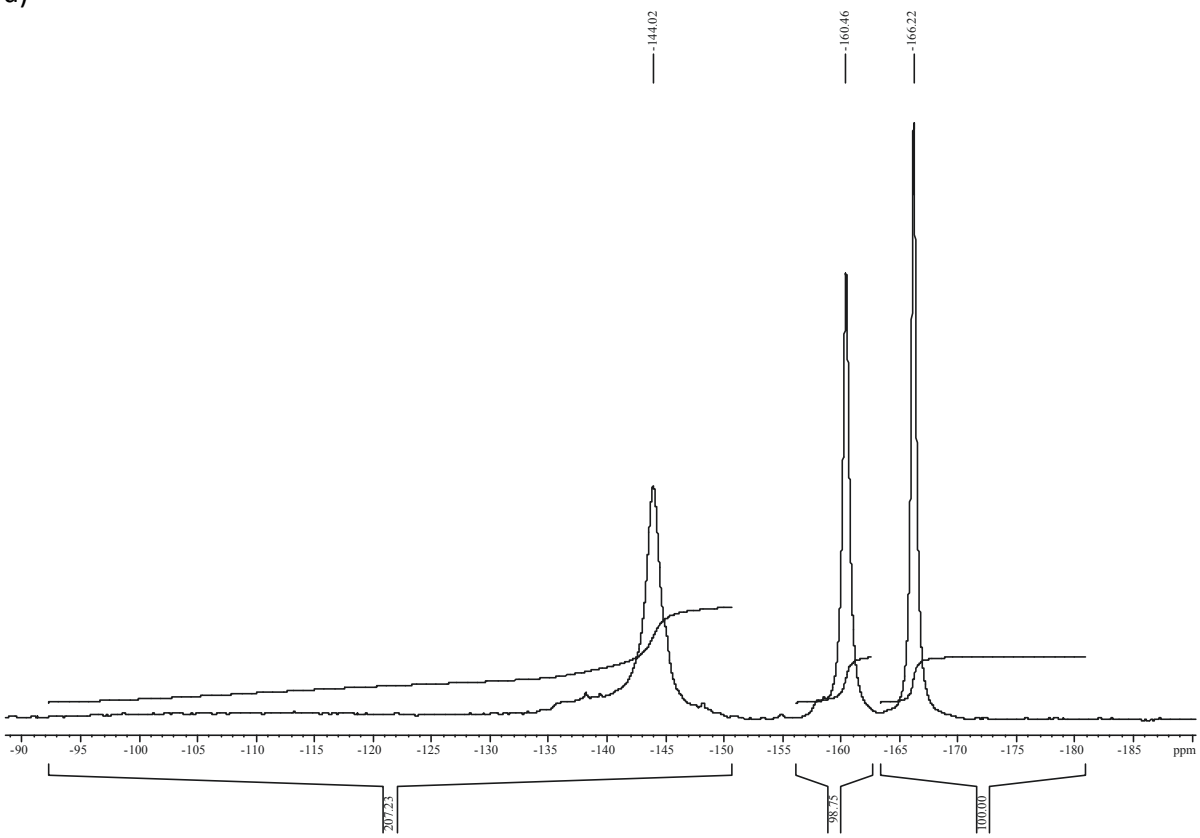
Unexpected findings in a simple metathesis reaction of europium and ytterbium diiodides with perfluorinated mercaptobenzothiazolates of alkali metals

Liubov I. Silantyeva,[a] Vasily A. Ilichev,*[a] Andrey S. Shavyrin,[a] Artem N. Yablonskiy,[b] Roman V. Rumyantcev,[a] Georgy K. Fukin,[a] and Mikhail N. Bochkarev*[a]

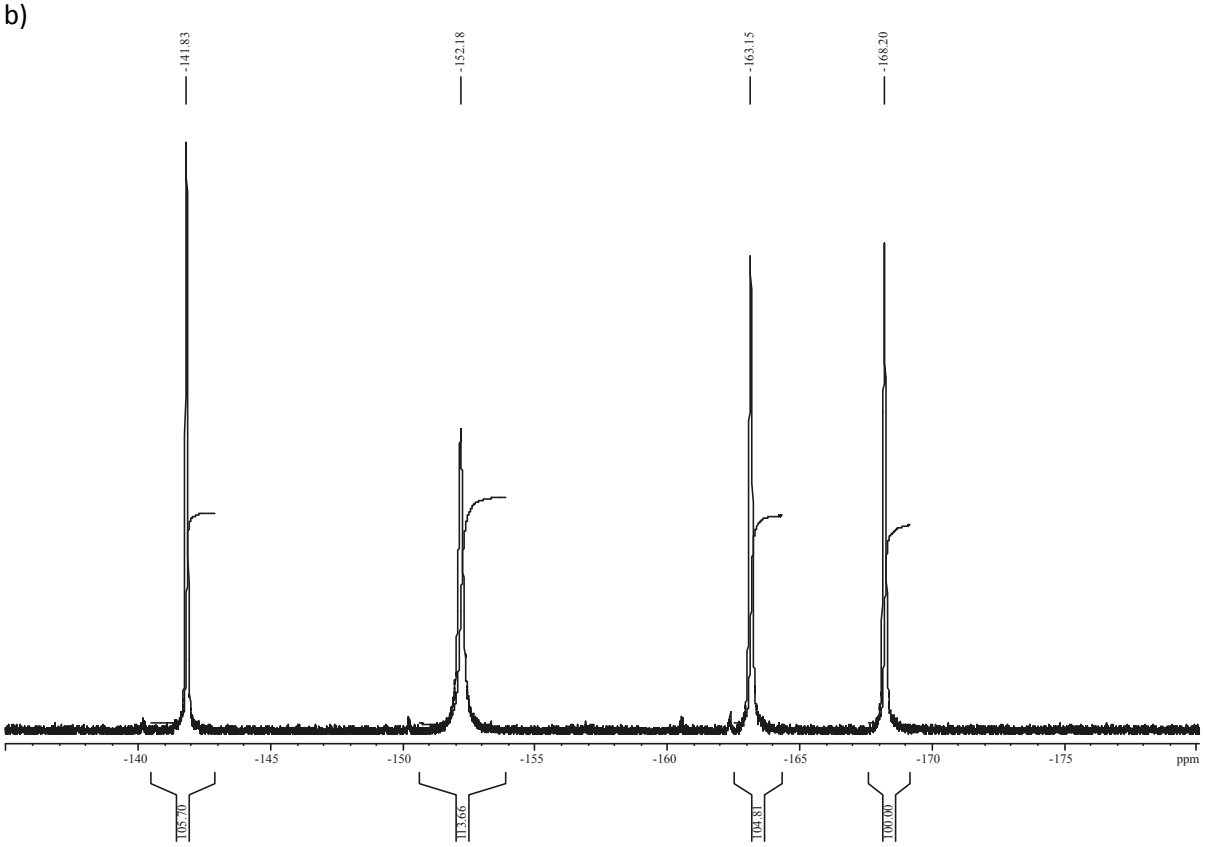
a G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina 49, 603950 Nizhny Novgorod, Russian Federation.

b Institute for Physics of Microstructures of Russian Academy of Sciences, 7 ul. Akademicheskaya, 603950 Nizhny Novgorod, Russian Federation.

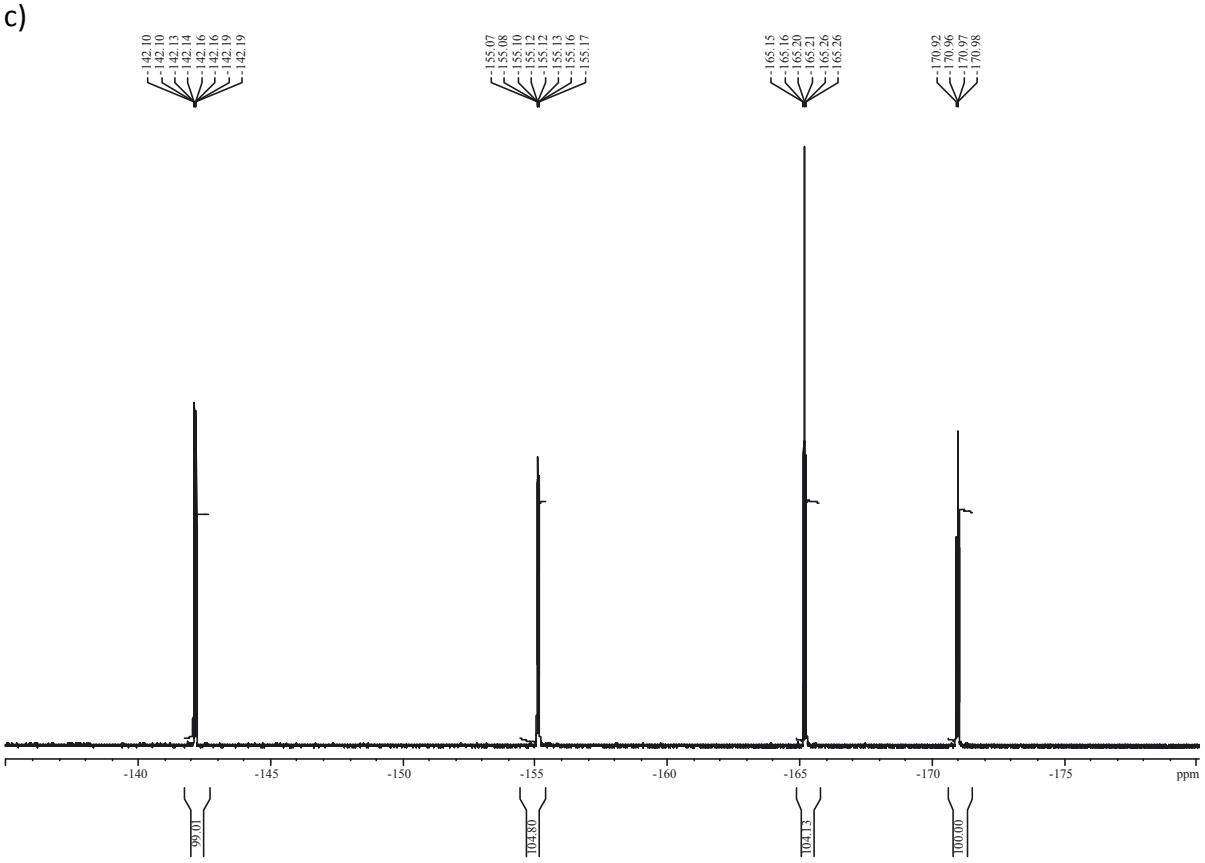
a)



b)


-141.83
-152.18
-163.15
-168.20
-140
-145
-150
-155
-160
-165
-170
-175
ppm
105.70
113.66
104.81
100.00

c)


-142.10
-142.10
-142.13
-142.14
-142.16
-142.16
-142.19
-142.19
-155.07
-155.08
-155.10
-155.12
-155.12
-155.13
-155.16
-155.17
-165.15
-165.16
-165.20
-165.21
-165.26
-165.26
-170.92
-170.96
-170.97
-170.98
-140
-145
-150
-155
-160
-165
-170
-175
ppm
99.01
104.80
104.13
100.00

d)

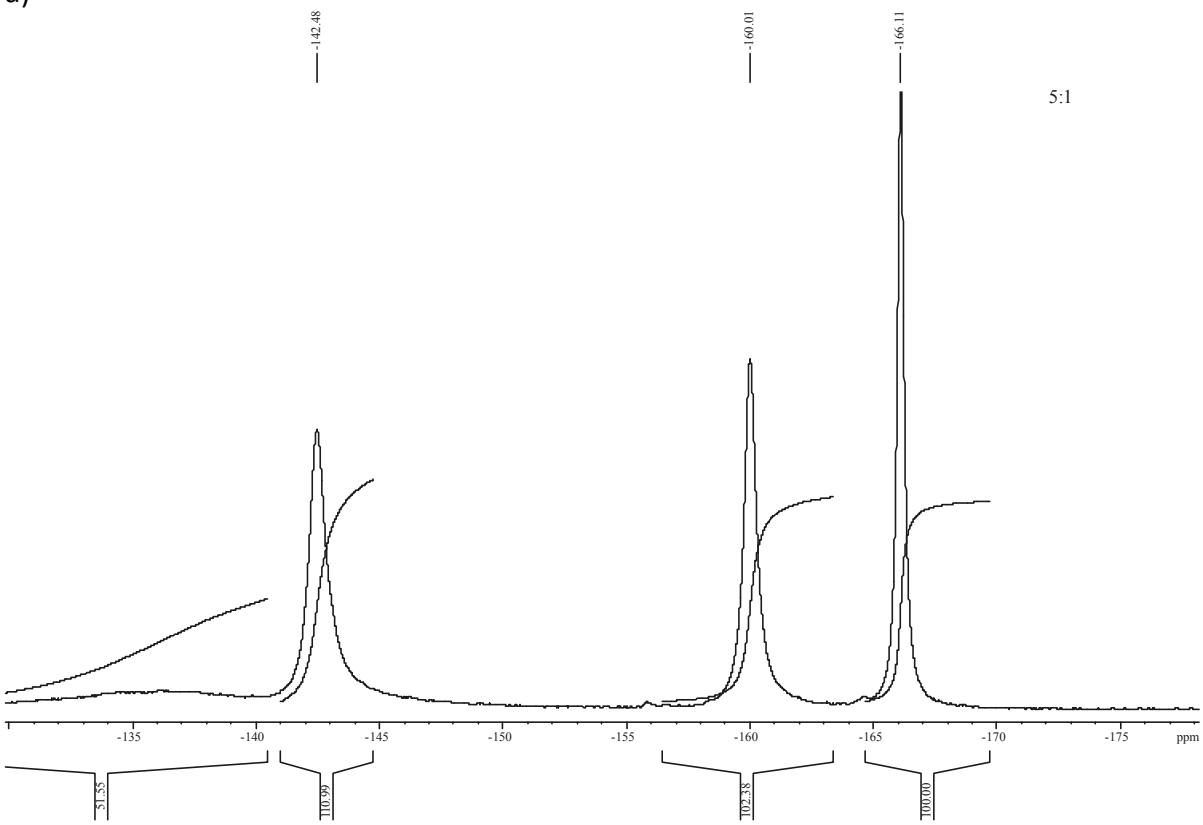


Figure 1S. ^{19}F NMR spectra of compounds **1** (a), **2** (b), **3** (c) and solution **A** (d). Solvent – DME.

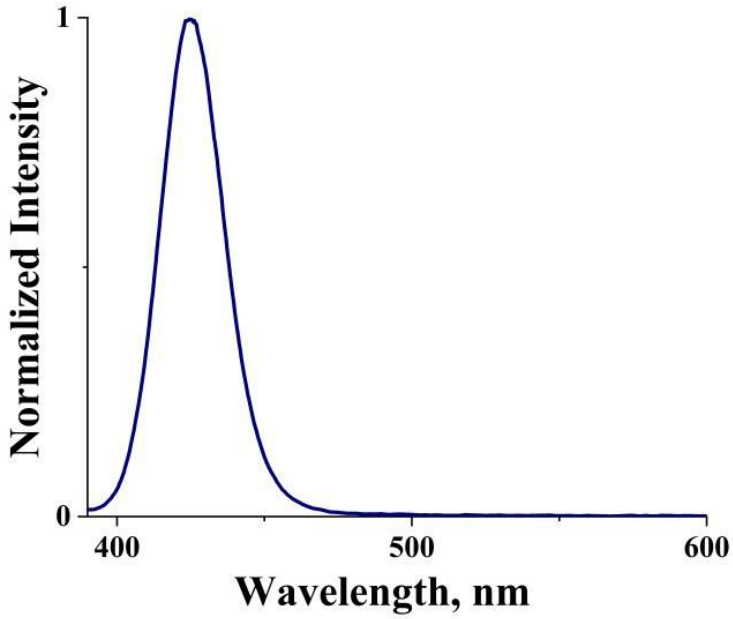


Figure 2S. PL spectrum of crystalline $EuI_2(DME)_3$. Excitation – 365 nm UV LED.

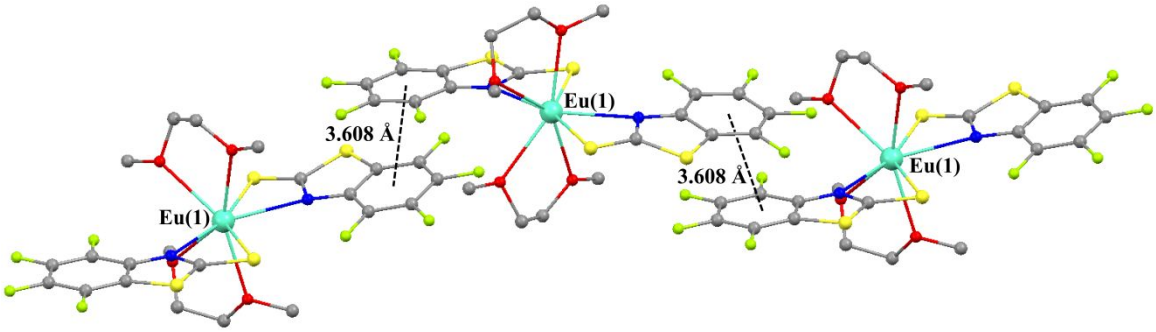


Figure 3S. Fragment of crystal packing of complex **1**.

Table 1S. The main distances [Å] in complexes **1**, $\mathbf{1}_{inv}$, $\mathbf{1}_{isol}$ (Ln = Eu) and **2**, $\mathbf{2}_{inv}$, $\mathbf{2}_{isol}$ (Ln = Yb).

Bond	**1**, Å	$\mathbf{1}_{inv}$, Å	$\mathbf{1}_{isol}$, Å	**2**, Å	$\mathbf{2}_{inv}$, Å	$\mathbf{2}_{isol}$, Å
Ln(1)-S(1)	2.9944(9)	2.99460(16)	3.0940	2.9465(19)	2.945(2)	3.0671
Ln(1)-S(3)	3.0439(8)	3.0411(9)	3.0456	2.9483(18)	2.9503(19)	3.0470
Ln(1)-N(1)	2.739(3)	2.7477(4)	2.7003	2.595(6)	2.608(6)	2.4751
Ln(1)-N(2)	2.679(3)	2.6856(5)	2.7348	2.673(5)	2.673(5)	2.5022
Ln(1)-O(1)	2.61(2)	2.5914(4)	2.6219	2.487(5)	2.493(5)	2.4438
Ln(1)-O(2)	2.678(2)	2.6864(4)	2.6944	2.499(5)	2.505(5)	2.5155
Ln(1)-O(3)	2.705(2)	2.7039(4)	2.6145	2.566(5)	2.570(5)	2.4826
Ln(1)-O(4)	2.537(2)	2.5261(11)	2.6219	2.464(5)	2.468(5)	2.4854
S(1)-C(1)	1.697(3)	1.6974(9)	1.7095	1.691(7)	1.680(7)	1.7061
S(2)-C(1)	1.771(3)	1.7718(9)	1.7971	1.778(7)	1.773(7)	1.7968
S(2)-C(2)	1.725(3)	1.7205(9)	1.7478	1.748(8)	1.743(8)	1.7521
S(3)-C(8)	1.690(3)	1.6881(10)	1.7064	1.665(8)	1.652(8)	1.7074
S(4)-C(8)	1.769(3)	1.7645(9)	1.7984	1.784(7)	1.777(7)	1.7958
S(4)-C(9)	1.727(3)	1.7232(10)	1.7470	1.740(7)	1.739(8)	1.7504
N(1)-C(1)	1.324(4)	1.3228(14)	1.3286	1.325(9)	1.329(8)	1.3279
N(1)-C(3)	1.391(4)	1.3799(13)	1.3809	1.379(9)	1.369(8)	1.3772
N(2)-C(8)	1.327(4)	1.3296(14)	1.3319	1.333(9)	1.346(8)	1.3280
N(2)-C(10)	1.370(4)	1.3619(14)	1.3814	1.377(9)	1.382(8)	1.3787
F-C	1.331(4) ÷ 1.346(4)	1.3238(13) ÷ 1.3479(13)	1.3387 ÷ 1.3525	1.335(8) ÷ 1.353(9)	1.324(8) ÷ 1.341(8)	1.3405 ÷ 1.3501

Table 2S. The main topological characteristics in the coordination sphere of the Ln atoms in complexes **1**$_{isol}$, **2**$_{isol}$ (DFT data) and **1**$_{inv}$, **2**$_{inv}$ (molecular invariom data).

Bonds	**1**$_{isol}$ (Eu)	**1**$_{inv}$ (Eu)	**2**$_{isol}$ (Yb)	**2**$_{inv}$ (Yb)	Bonds	**1**$_{isol}$ (Eu)	**1**$_{inv}$ (Eu)	**2**$_{isol}$ (Yb)	**2**$_{inv}$ (Yb)
v(**r**), a.e.					$\nabla^2\rho$(**r**), a.e.				
Ln(1)-S(1)	-0.012	-0.026	-0.012	-0.020	Ln(1)-S(1)	0.072	0.054	0.063	0.078
Ln(1)-S(3)	-0.014	-	-0.012	-0.019	Ln(1)-S(3)	0.078	-	0.066	0.076
Ln(1)-N(1)	-0.021	-0.020	-0.036	-0.027	Ln(1)-N(1)	0.116	0.088	0.180	0.120
Ln(1)-N(2)	-0.019	-0.026	-0.033	-0.023	Ln(1)-N(2)	0.107	0.113	0.167	0.103
Ln(1)-O(1)	-0.024	-0.037	-0.035	-0.034	Ln(1)-O(1)	0.133	0.160	0.188	0.160
Ln(1)-O(2)	-0.020	-0.023	-0.028	-0.033	Ln(1)-O(2)	0.110	0.109	0.152	0.154
Ln(1)-O(3)	-0.025	-0.020	-0.031	-0.027	Ln(1)-O(3)	0.137	0.098	0.168	0.130
Ln(1)-O(4)	-0.022	-0.041	-0.030	-0.037	Ln(1)-O(4)	0.122	0.174	0.165	0.169
ρ(**r**), a.e.					h_e(**r**), a.e.				
Ln(1)-S(1)	0.020	0.035	0.019	0.027	Ln(1)-S(1)	0.003	-0.006	0.002	0.000
Ln(1)-S(3)	0.023	-	0.019	0.026	Ln(1)-S(3)	0.003	-	0.002	0.000
Ln(1)-N(1)	0.028	0.026	0.040	0.031	Ln(1)-N(1)	0.004	0.001	0.005	0.001
Ln(1)-N(2)	0.026	0.030	0.038	0.027	Ln(1)-N(2)	0.004	0.001	0.005	0.001
Ln(1)-O(1)	0.029	0.037	0.037	0.034	Ln(1)-O(1)	0.005	0.001	0.006	0.003
Ln(1)-O(2)	0.025	0.027	0.032	0.033	Ln(1)-O(2)	0.004	0.002	0.005	0.003
Ln(1)-O(3)	0.031	0.025	0.035	0.029	Ln(1)-O(3)	0.004	0.002	0.005	0.003
Ln(1)-O(4)	0.027	0.040	0.033	0.036	Ln(1)-O(4)	0.004	0.001	0.005	0.003

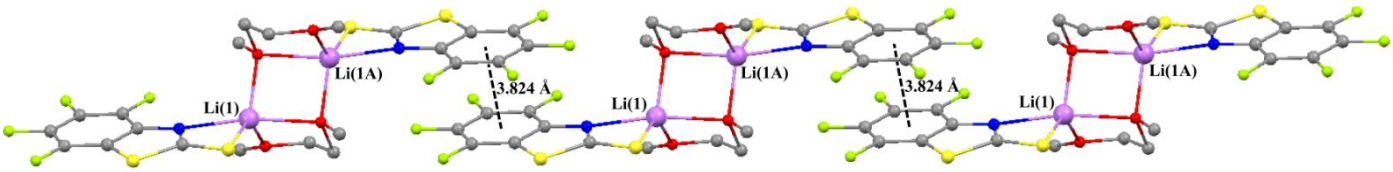
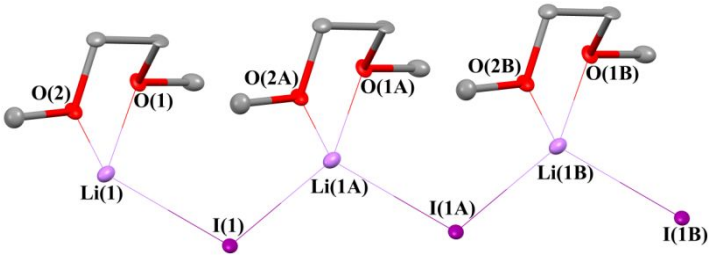
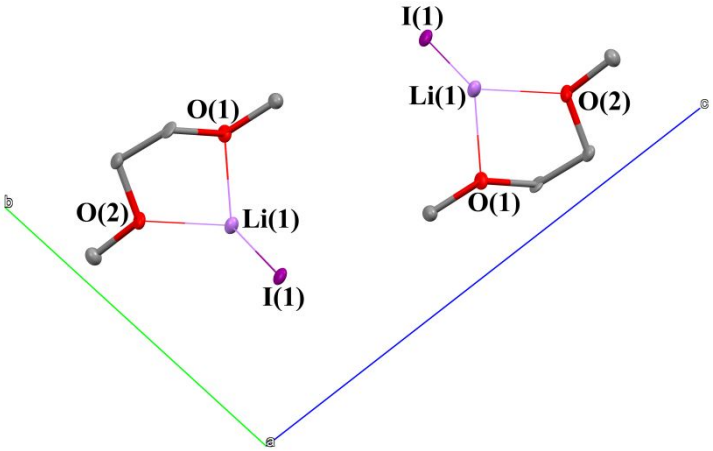


Figure 4S. Fragment of crystal packing of complex **3**.



a



b

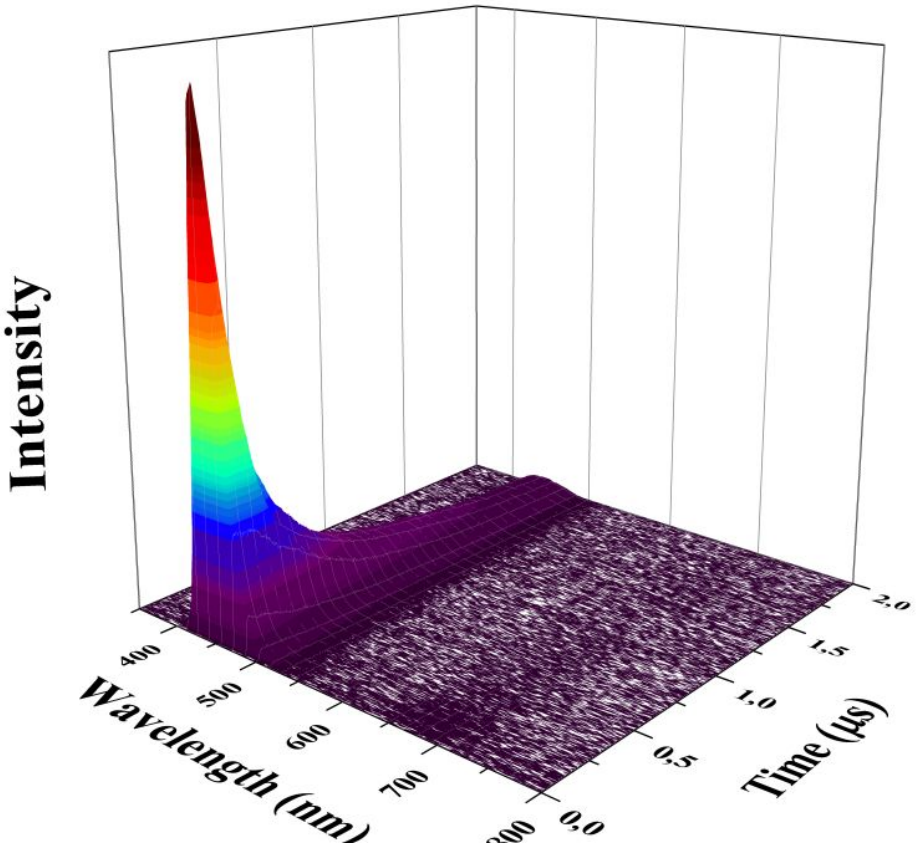
Figure 5S. Fragment of molecular chain (**a**) and fragment of crystal packing along *a* crystal axes (**b**) of complex **4**. The probability ellipsoids are drawn at the 30% level. The hydrogen atoms are omitted for clarity.

Selected distances [Å] and angles [°]: Li(1)-O(2) 1.964(15), Li(1)-O(1) 1.998(15), Li(1)-I(1) 2.674(14), Li(1)-I(1A) 2.750(13); O(2)-Li(1)-O(1) 83.1(6), O(2)-Li(1)-I(1) 113.6(6), O(1)-Li(1)-I(1) 125.8(6), O(2)-Li(1)-I(1A) 113.8(5), O(1)-Li(1)-I(1A) 104.5(6), I(1)-Li(1)-I(1A) 112.8(5), Li(1)-I(1)-Li(1A) 112.8(5).

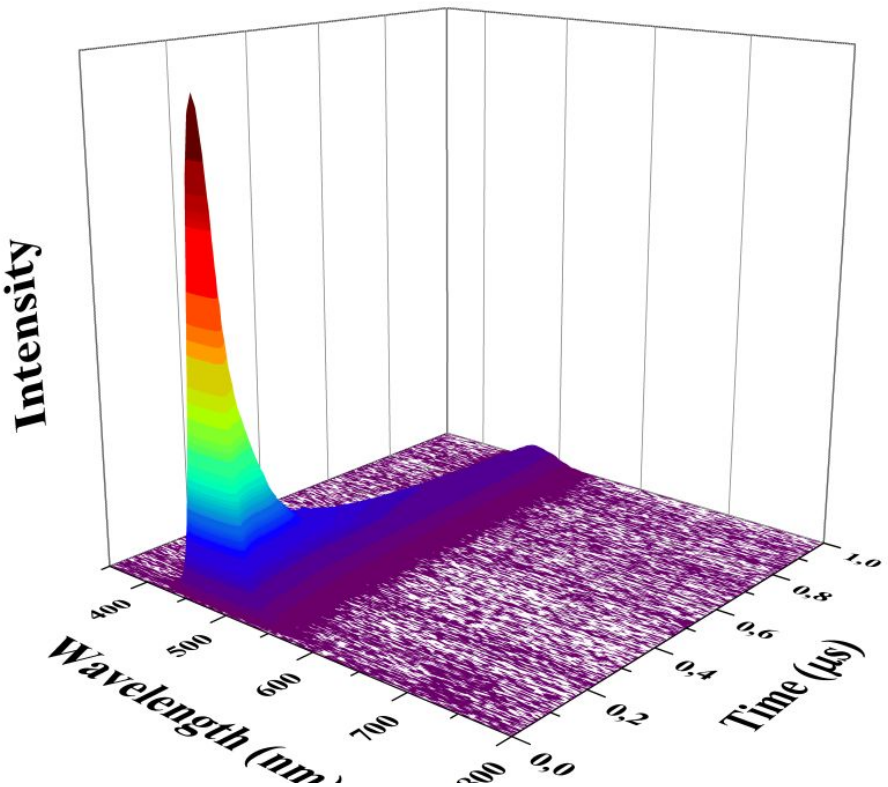
Table 1x. X-ray data collection and refinement parameters for **1**-**3** and $[LiI(DME)]_n$.

Complex	**1**	**2**	**3**	$[LiI(DME)]_n$
Empirical formula	$C_{22}H_{20}EuF_8N_2O_4S_4$	$C_{22}H_{20}F_8N_2O_4S_4Yb$	$C_{22}H_{20}F_8Li_2N_2O_4S_4$	$C_4H_{10}ILiO_2$
Formula weight	808.60	829.68	670.52	223.96
T (K)	100(2)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$P2_12_12_1$	$P2_1/n$	P-1	P-1
Unit cell dimensions				
a (Å)	8.2564(2)	10.1065(5)	7.2026(2)	4.5176(7)
b (Å)	16.2975(4)	22.7024(10)	8.1457(3)	7.5494(11)
c (Å)	20.7578(5)	12.4265(6)	12.7563(4)	11.7399(17)
α (°)	90	90	72.3210(10)	99.678(3)
β (°)	90	91.9246(14)	85.3310(10)	92.977(3)
γ (°)	90	90	72.2750(10)	90.010(3)
V ($Å^3$)	2793.14(12)	2849.6(2)	679.17(4)	394.14(10)
Z	4	4	1	2
$D_{calc.}$($g \cdot cm^{-3}$)	1.923	1.934	1.639	1.887
Absorption coefficient, μ (mm^{-1})	2.631	3.660	0.439	3.983
F (000)	1588	1616	340	212
Crystal size (mm^3)	0.41 × 0.28 × 0.26	0.28 × 0.08 × 0.03	0.21 × 0.11 × 0.03	0.28 × 0.07 × 0.06
Range for data collection, θ (°)	2.326 ÷ 39.046	2.431 ÷ 26.500	2.746 ÷ 29.999	2.996 ÷ 25.994
Limiting indices	$-14 \le h \le 14$, $-28 \le k \le 28$, $-36 \le l \le 36$	$-12 \le h \le 12$, $-28 \le k \le 27$, $-15 \le l \le 15$	$-10 \le h \le 10$, $-11 \le k \le 11$, $-17 \le l \le 17$	$-5 \le h \le 5$, $-9 \le k \le 9$, $-14 \le l \le 14$
Reflections collected/unique	65554 / 16176	22352 / 5903	9191 / 3949	3614 / 1553
$R_{(int)}$	0.0312	0.0660	0.0133	0.0594
Data/restraints/parameters	16176 / 55 / 415	5903 / 0 / 374	3949 / 0 / 192	1553 / 6 / 75
S	1.045	1.068	1.050	1.058
Final R indices [I > 2σ(I)]	R_1 = 0.0305, wR_2 = 0.0654	R_1 = 0.0517, wR_2 = 0.0916	R_1 = 0.0233, wR_2 = 0.0609	R_1 = 0.0663, wR_2 = 0.1753
R indices (all data)	R_1 = 0.0320, wR_2 = 0.0659	R_1 = 0.0780, wR_2 = 0.0968	R_1 = 0.0261, wR_2 = 0.0622	R_1 = 0.0699, wR_2 = 0.1782
Largest diff. peak/hole (e $Å^{-3}$)	1.312 / -3.283	1.519 / -2.649	0.357 / -0.345	4.796 / -4.383

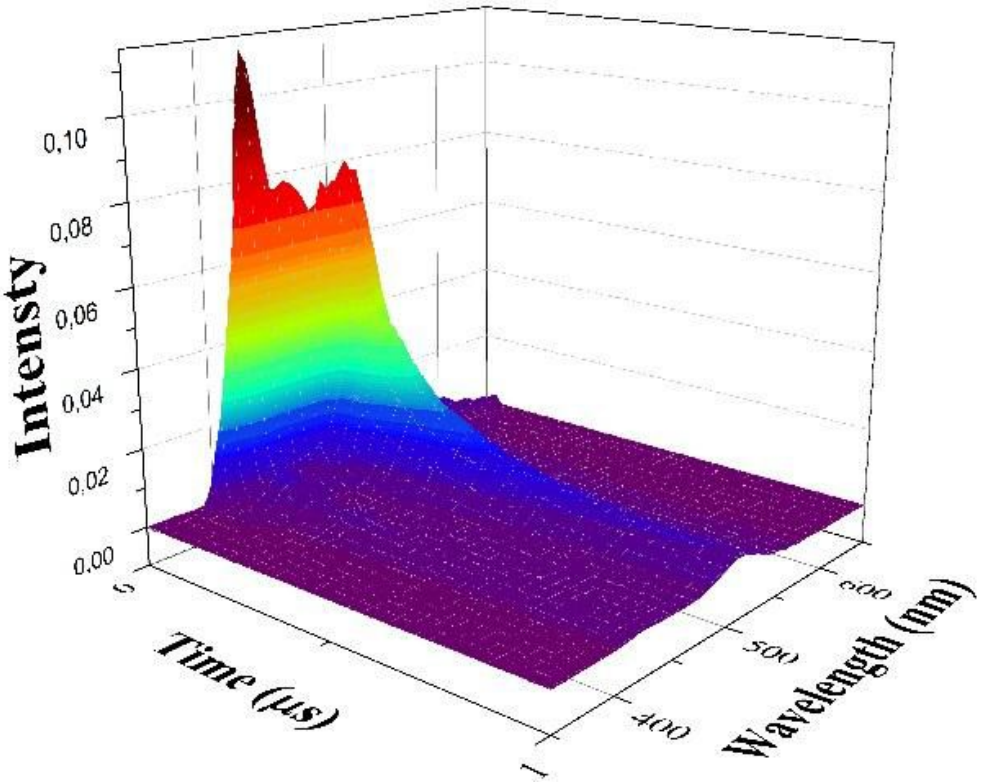
a)


Intensity
Wavelength (nm)
400
500
600
700
Time (µs)
0,0
0,5
1,0
1,5
2,0

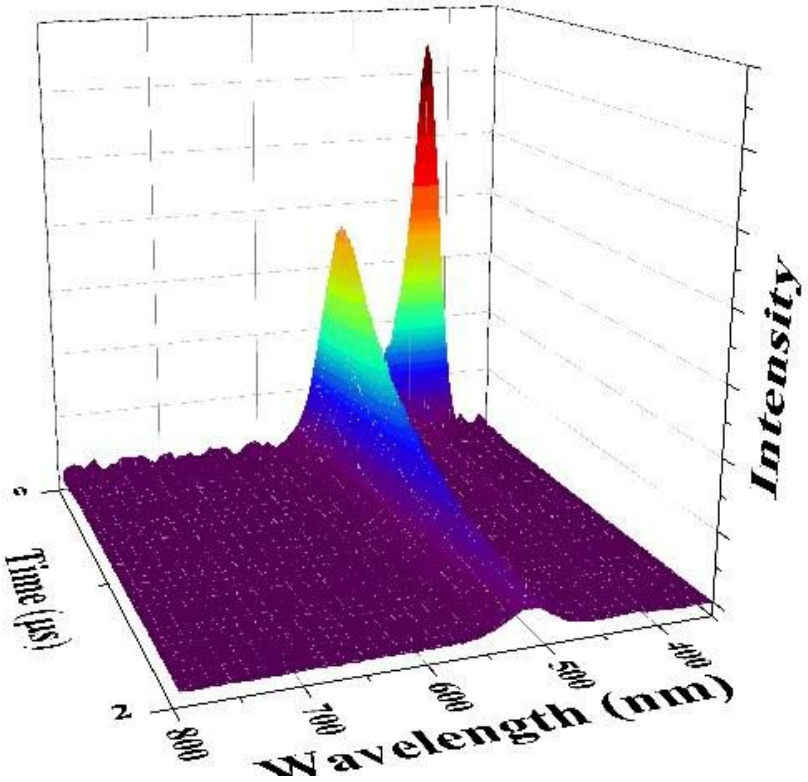
b)


Intensity
Wavelength (nm)
400
500
600
700
Time (µs)
0,0
0,2
0,4
0,6
0,8
1,0

c)


Intensty
0,10
0,08
0,06
0,04
0,02
0,00
Time (µs)
Wavelength (nm)
400
500
600

d)


Intensity
Time (µs)
Wavelength (nm)
800
700
600
500
400

e)

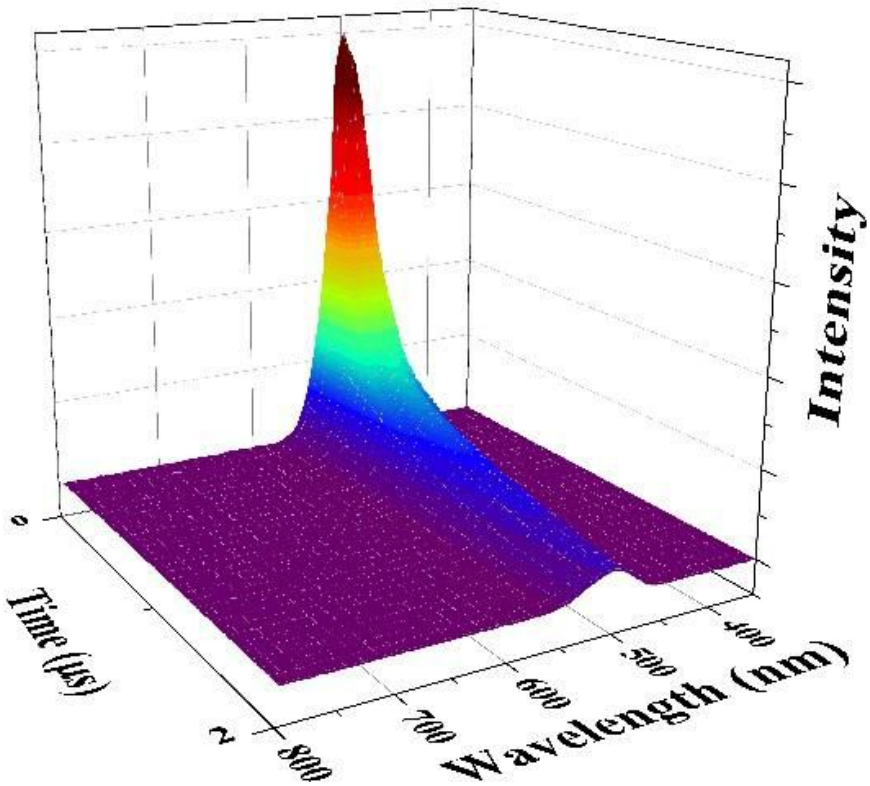


Figure 6S. Time-resolved PL spectra of $EuI_2(THF)_2$ in THF solution (a), solid state (b) and DME solution (c); time-resolved PL spectra of solution **A** (d) and solid **B** (e). Excitation – Nd:YAG laser at 355 nm (pulse duration ~ 5 ns).