Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Tuning the luminescence efficiency by perfluorination of side chains in Eu^{3+} complexes with β-diketones of thiophene series.

Evgeniya A. Varaksina,[*a] Mikhail A. Kiskin,[b] Konstantin A. Lyssenko,[c] Lada N. Puntus,[d] Vladislav M. Korshunov,[ae], Gustavo S. Silva[f], Ricardo O. Freire[f] and Ilya V. Taydakov,[*a]

[a] *P. N. Lebedev Physics Institute of the Russian Academy of Sciences, Leninsky prospect 53, 119991 Moscow, Russia. E-mail: evgeniya.a.varaksina@phystech.edu, taidakov@gmail.ru*
[b] *N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Leninsky Prosp. 31, 119991 Moscow, Russian Federation.*
[c] *National research university higher school of economics, 101000, Myasnitskaya st., 20, Moscow, Russia.*
[d] *V.A. Kotel'nikov Institute of Radioengineering and Electronics, Russian Academy of Sciences, 11-7 Mokhovaya Str., Moscow, 125009, Russian Federation.*
[e] *Bauman Moscow State Technical University, 2-ya Baumanskaya Str. 5/1, 105005, Moscow, Russia.*
[f] *Pople Computational Chemistry Laboratory, Departamento de Química, Universidade Federal de Sergipe, 49.100-000 São Cristóvão,- SE, Brazil.*

Supporting Information

Preparation of complexes [Gd(L)$_3$]·nMeOH. General method.

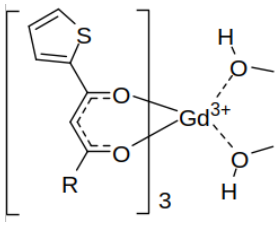


Fig. S1 Chemical structure of [Gd(L)$_3$]·nMeOH (R=CHF_2, C_3F_7-C_5F_{11})

A solution of $GdCl_3 \cdot 6H_2O$ (111 mg, 0.3 mmol) in 2 mL of deionized water was treated in a plastic centrifuge tube with 0.3 mL of concentrated aqueous ammonia solution and the slurry was shaken mechanically in a closed tube for 2 min. Then 10 mL of deionized water was added and the suspension was centrifuged at 11000 rpm for 10 min. The supernatant was discarded, and the precipitate was washed twice with 10 mL of deionized water and three times with 10 mL of MeOH. Each time the precipitate was first re-suspended in the washing liquid and then centrifuged at 11000 rpm for 10 min. A corresponding diketone (0.9 mmol) was dissolved in 10 mL of anhydrous MeOH with stirring and heating. This solution was added to the solid Gd(OH)$_3$·nMeOH in the same centrifuge tube, and the closed tube was shaken at 45°C until a clear solution was obtained. This solution was centrifuged at 11000 rpm for 10 min and the supernatant was transferred into a Schlenk tube and evaporated at 40°C under reduced pressure. The resulting solid was redissolved in 10 mL of anhydrous MeOH and evaporated again. This operation was repeated twice, and the resulting glass was finally dried at 10^{-3} Torr and 45°C to a constant weight. It was stored in dry nitrogen atmosphere to prevent MeOH/H_2O exchange due to air moisture.

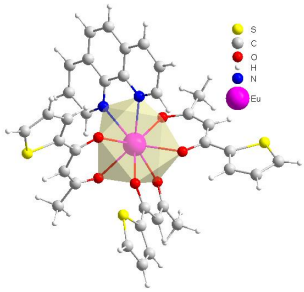
[Gd(ThCHF$_2$)$_3$]·nMeOH (**2d**). Brown glass. Yield 0.23 g. For $C_{26}H_{23}F_6GdO_8S_3$ ([Gd(ThCHF$_2$)$_3$(MeOH)$_2$], FW 830.89) calcd.(%) C, 37.58; H, 2.78; Gd, 18.93; found (%) C, 38.31; H, 3.23; Gd, 17.88; n≈1.3.

[Gd(ThC$_3$F$_7$)$_3$]·nMeOH (**5d**). Yellow glass. Yield 0.345 g. For $C_{32}H_{20}F_{21}GdO_8S_3$ ([Gd(ThC$_3$F$_7$)$_3$(MeOH)$_2$], FW 1184.91) calcd.(%) C, 37.44; H, 1.70; F, 33.67; Gd, 13.23; found (%) C, 33.36; H, 2.39; F, 31.34; Gd, 12.42; n≈2.5.

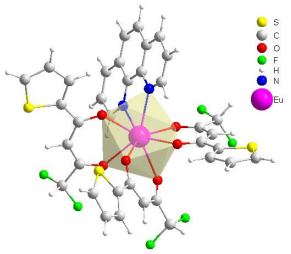
[Gd(ThC$_4$F$_9$)$_3$]·nMeOH (**6d**). Red-brown glass. Yield 0.336 g. For $C_{35}H_{20}F_{27}GdO_8S_3$ ([Gd(ThC$_4$F$_9$)$_3$(MeOH)$_2$], FW 1334.94) calcd.(%) C, 31.49; H, 1.51; F, 38.43; Gd, 11.78; found (%) C, 33.38; H, 2.35; F, 37.40; Gd, 11.49; n≈3.1.

[Gd(ThC$_5$F$_{11}$)$_3$]·nMeOH (**7d**). Brown glass. Yield 0.374 g. For $C_{38}H_{20}F_{33}GdO_8S_3$ ([Gd(ThC$_5$F$_{11}$)$_3$(MeOH)$_2$], FW 1484.95) calcd.(%) C, 30.78; H, 1.36; F, 42.22; Gd, 10.59; found (%) C, 31.44; H, 2.17; F, 38.96; Gd, 9.73; n≈3.8.

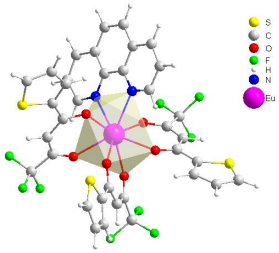
Optimized ground state geometries of 1a-10a calculated using RM1 model



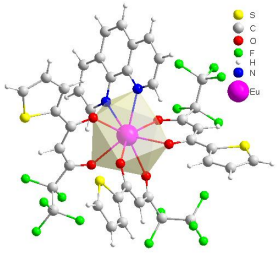
(a) 1a



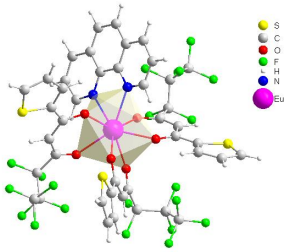
(b) 2a



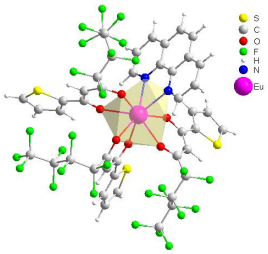
(c) 3a



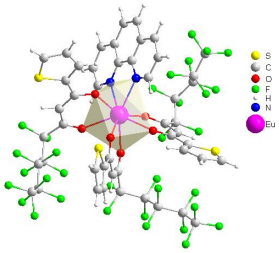
(d) 4a



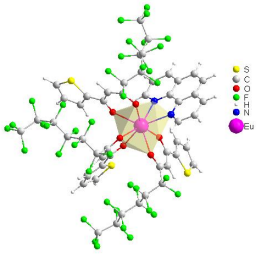
(e) 5a



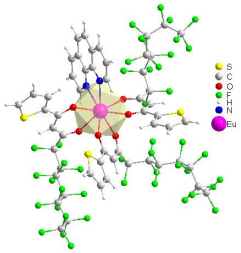
(f) 6a



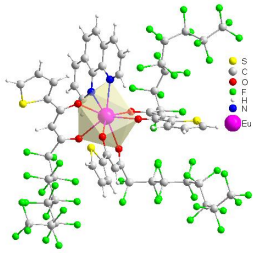
(g) 7a



(h) 8a



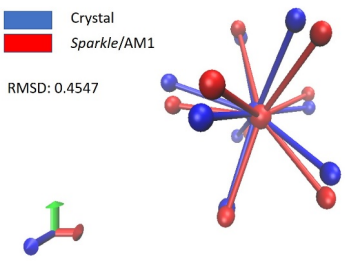
(i) 9a



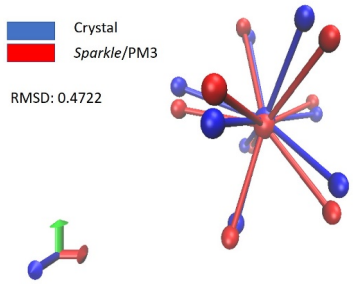
(j) 10a

Fig. S2 Optimized ground state geometries of **1a-10a** calculated using RM1 model

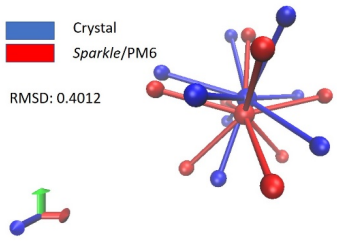
Sparkle/



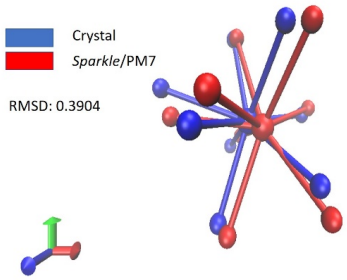
(a)



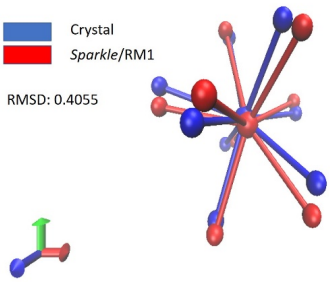
(b)



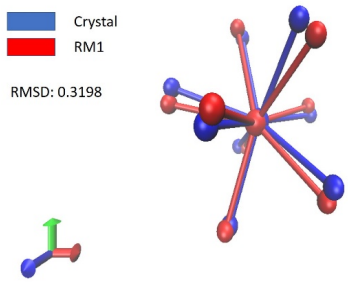
(c)



(d)

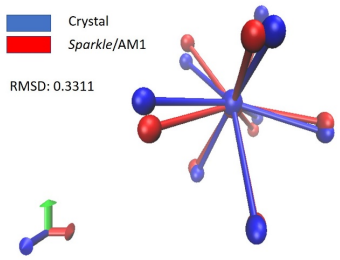


(e)

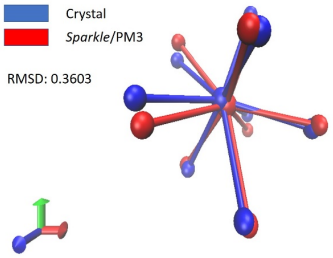


(f)

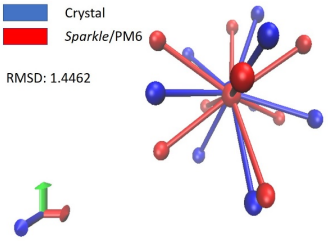
Fig. S3 Coordination polyhedra for complex **1a** (calculated and X-ray data).



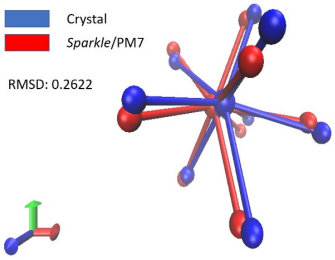
(a)



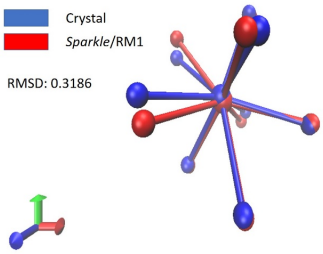
(b)



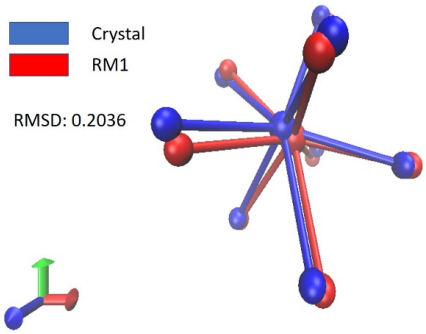
(c)



(d)

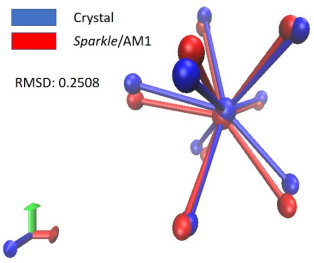


(e)

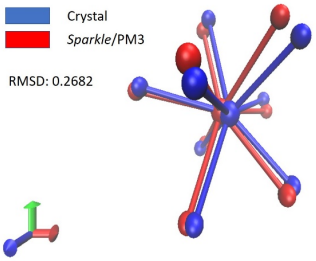


(f)

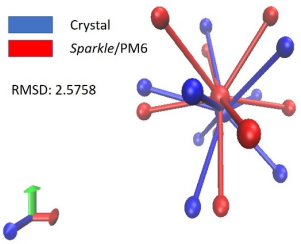
Fig. S4 Coordination polyhedra for complex **2a** (calculated and X-ray data).



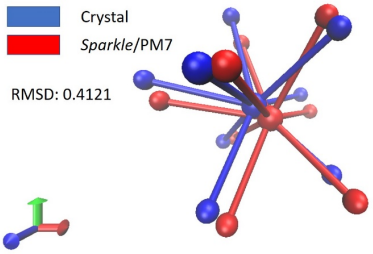
(a)



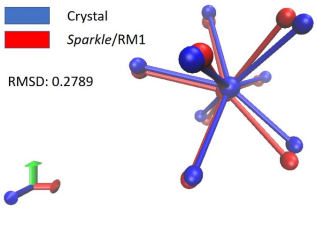
(b)



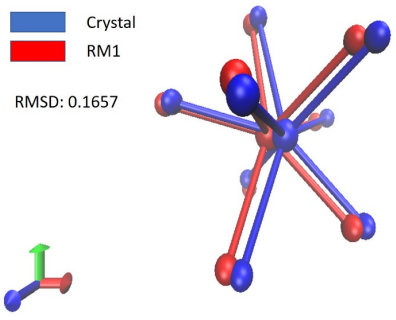
(c)



(d)



(e)



(f)

Fig. S5 Coordination polyhedra for complex **3a** (calculated and X-ray data).

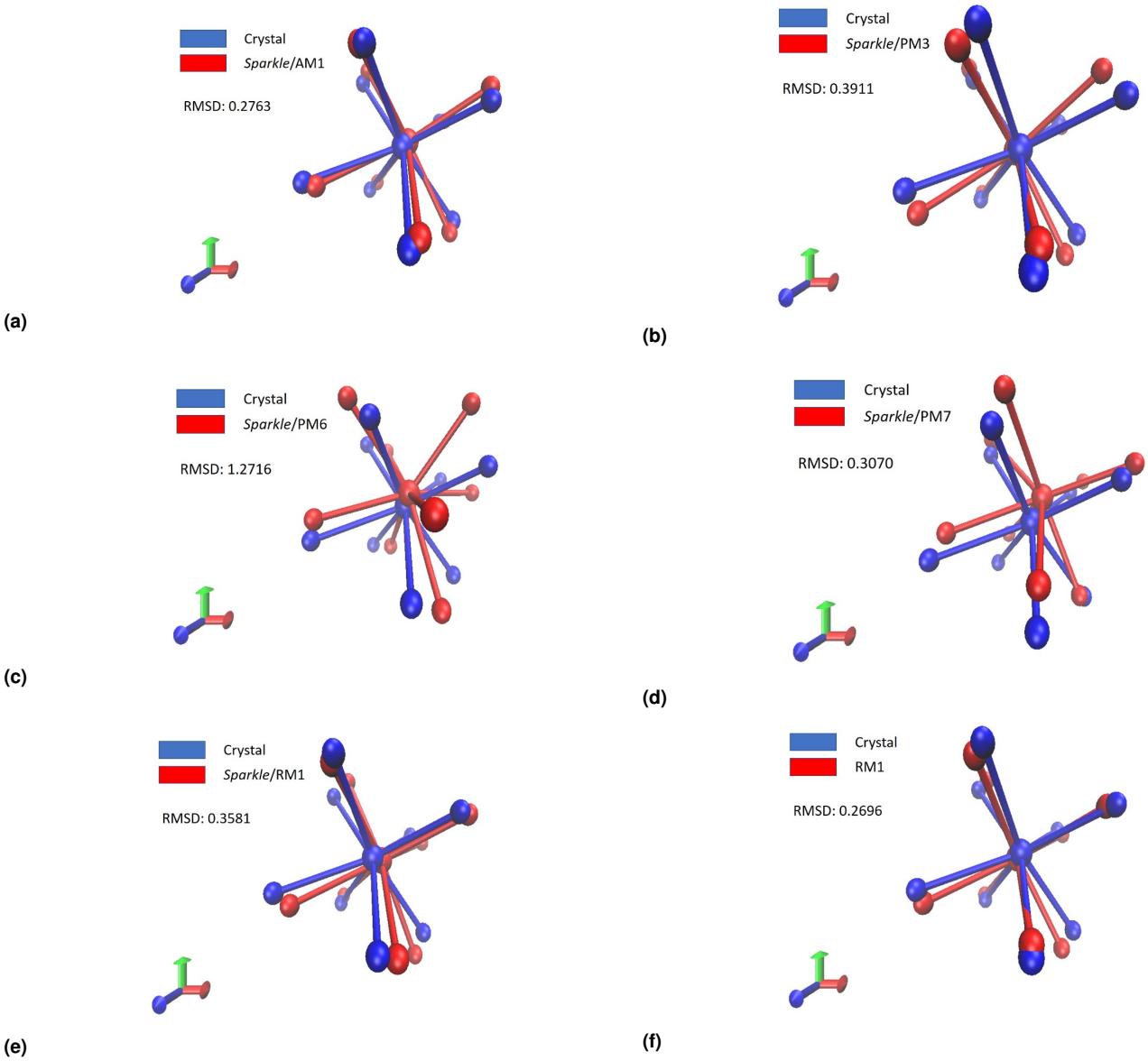


Fig. S6 Coordination polyhedra for complex **5a** (calculated and X-ray data).

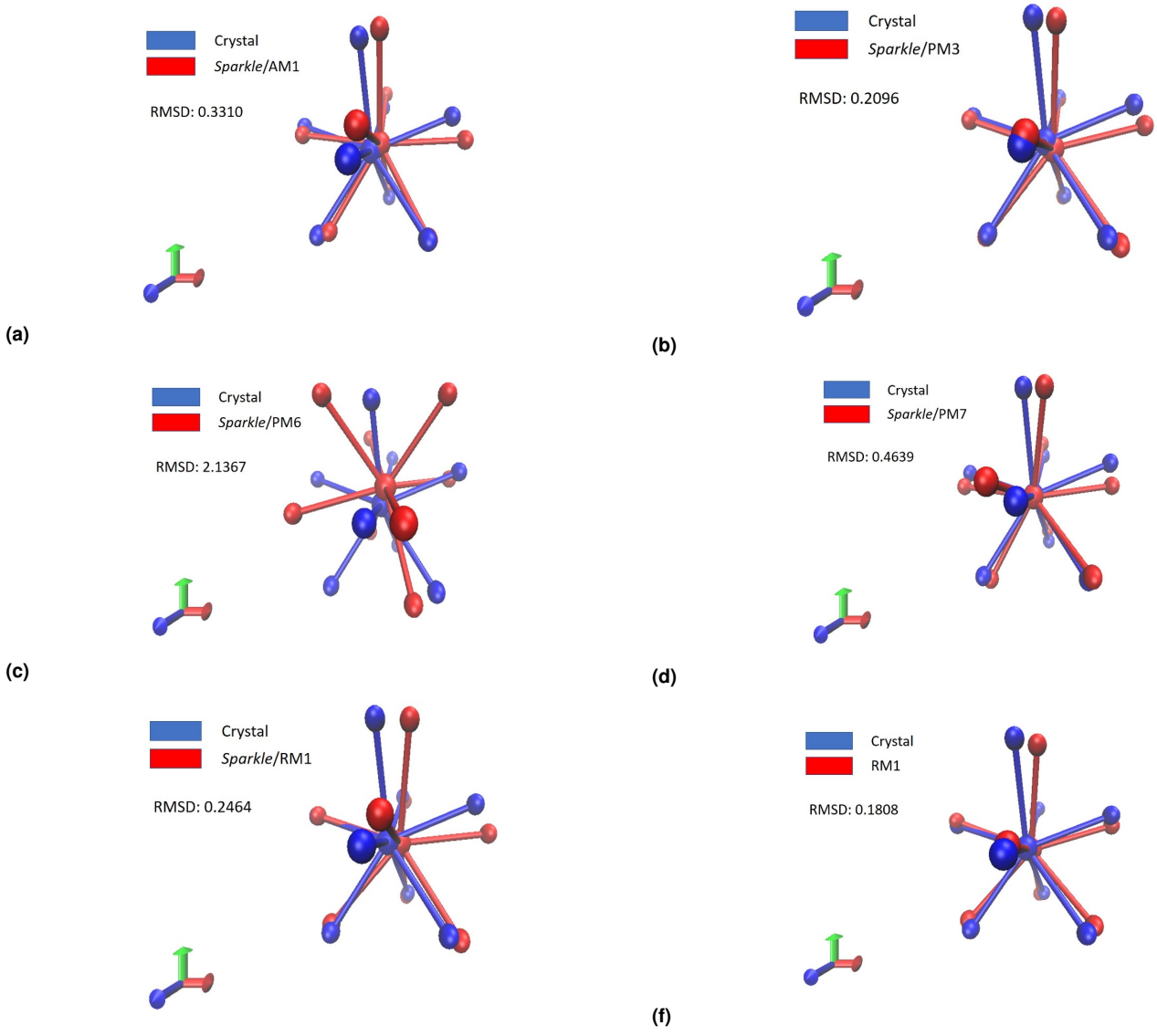


Fig. S7 Coordination polyhedra for complex **6a** (calculated and X-ray data).

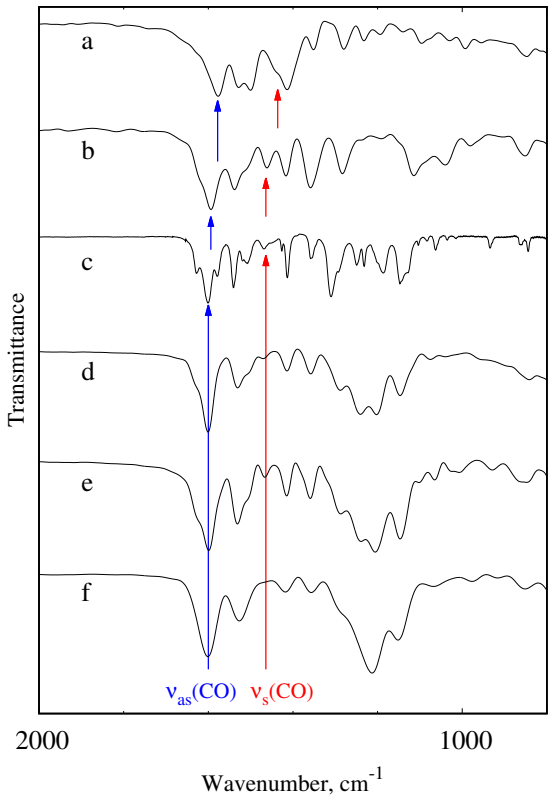


Fig. S8 FTIR-spectra of complexes in KBr **1a** (a), **2a** (b), **3a** (c), **8a** (d), **9a** (e) and **10a** (f).

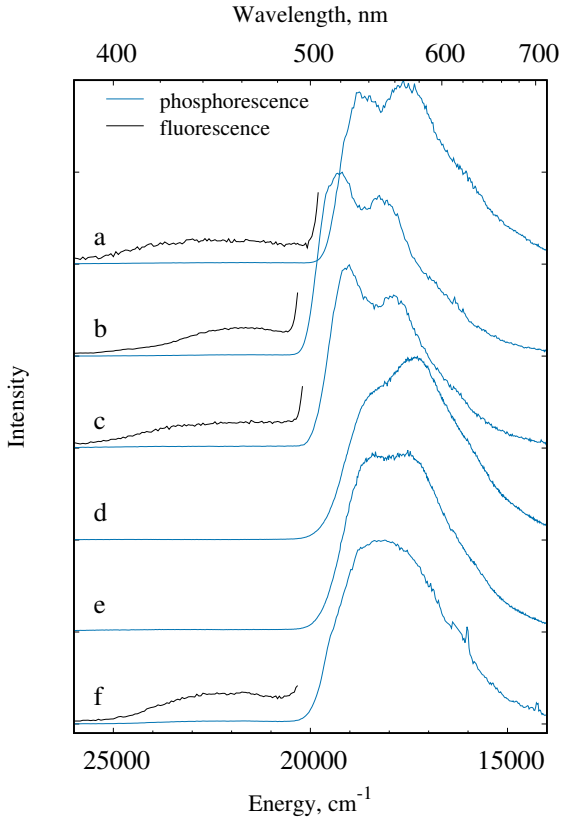
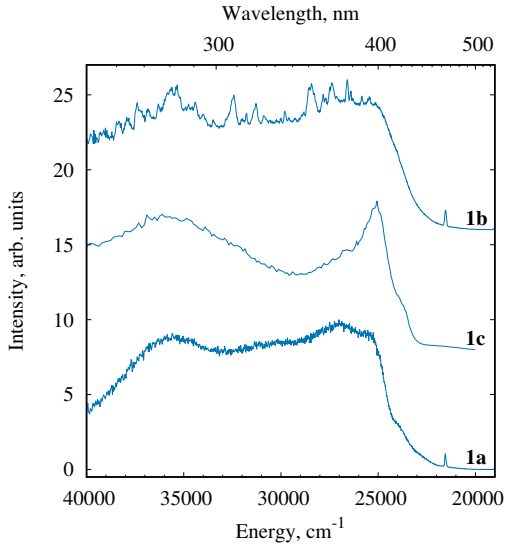
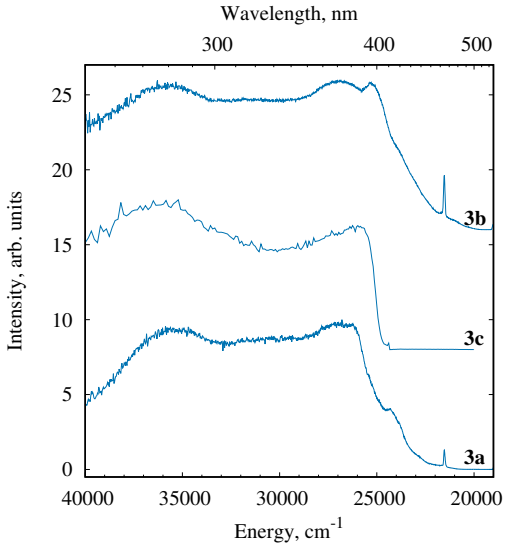


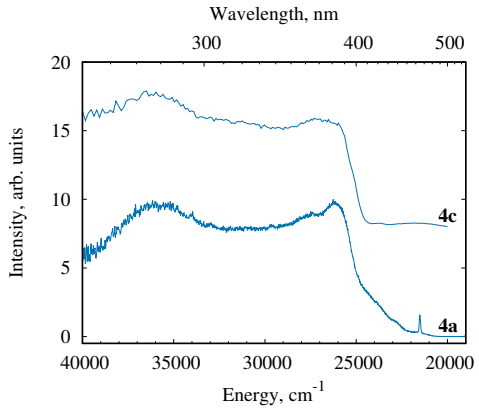
Fig. S9 Solid-state phosphorescence (blue line) and fluorescence (black line) spectra of **1c** (a), **3c** (b), **4c** (c), **8c** (d), **9c** (e) and **10c** (f) at λ_{ex} = 280 nm and T=77 K.



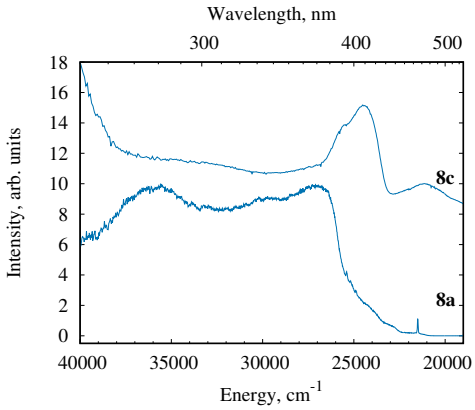
(a)



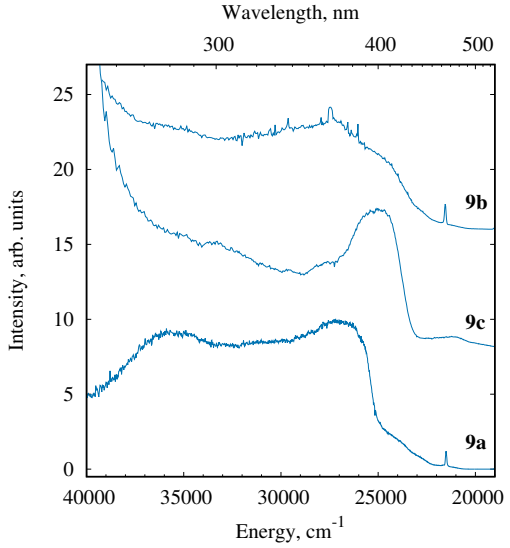
(b)



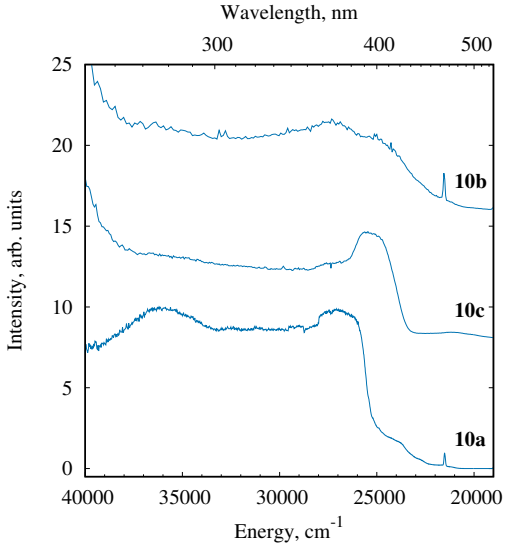
(c)



(d)



(e)



(f)

Fig. S10 Solid-state excitation spectra of Eu^{3+} and Gd^{3+} compounds.

Table S1 Selected crystal data and parameters for structure refinement of compounds **1a**-**3a**, **5a** and **6a**

	1a	**2a**	**3a**·Me_2CO	**5a**	**6a**
CCDC	2081275	2081276	2081277	2088575	2088576
Empirical formula	$C_{36}H_{29}EuN_2O_6S_3$	$C_{36}H_{23}EuF_6N_2O_6S_3$	$C_{39}H_{26}EuF_9N_2O_7S_3$	$C_{42}H_{20}EuF_{21}N_2O_6S_3$	$C_{45}H_{20}EuF_{27}N_2O_6S_3$
Formula weight	833.75	941.70	1053.76	1295.74	1445.77
T (K)	150(2)	150(2)	150(2)	120(2)	100(2)
Crystal system	triclinic	triclinic	monoclinic	orthorhombic	triclinic
Space group	P-1	P-1	$P2_1$	$Pbca$	P-1
Crystal size (mm)	$0.15\times0.10\times0.06$	$0.02\times0.02\times0.08$	$0.25\times0.20\times0.05$	$0.37\times0.31\times0.16$	$0.40\times0.27\times0.20$
a (Å)	9.1817(5)	9.4489(7)	9.8914(5)	20.6112(6)	15.2499(8)
b (Å)	13.0615(7)	13.2007(11)	10.6986(5)	17.9832(5)	15.6839(8)
c (Å)	15.0182(8)	14.8576(11)	38.1886(18)	25.1758(8)	22.6048(11)
α, °	96.107(2)	90.152(4)	90	90	78.9390(10)
β, °	92.850(2)	94.059(3)	89.992(2)	90	89.6640(10)
γ, °	104.079(2)	102.044(3)	90	90	79.5320(10)
V, Å^3	1731.72(16)	1807.6(2)	4041.3(3)	9331.5(5)	5215.5(5)
Z	2	2	4	8	4
D_{calc} (g·cm^{-3})	1.599	1.73	1.732	1.845	1.841
μ (mm^{-1})	2.04	1.988	1.801	1.612	1.469
θ range (°)	2.46-26.37	1.37-27.88	1.60-28.28	1.00-27.50	1.35-27.00
Range of h, k and l	-11→11 -16→16 -18→18	-12→12 -17→17 -17→19	-13→13 -14→14 -50→49	-26→26 -23→23 -32→32	-19→19 -20→20 -28→28
T_{min}/T_{max}	0.602/0.746	0.633/0.746	0.587/0.746	0.585/0.785	0.495/0.658
$F(000)$	836	932	2088	5072	2824
Number of parameters	436	494	1116	743	1594
Reflections collected	23879	16459	42018	78170	66431
Unique reflections	7066	8489	19911	10719	22729
Reflections with $I>2\sigma(I)$	6560	6035	16463	9531	16695
R_{int}	0.1447	0.0689	0.0442	0.0368	0.0381
$GooF$	1.053	1.016	1.105	1.1	0.997
$R_1(I>2\sigma(I))$	0.0484	0.064	0.0556	0.0704	0.0745
$wR_2(I>2\sigma(I))$	0.1215	0.1188	0.0914	0.1583	0.1831

Table S2 Selected distances (d, Å) and angles (ω, deg.) for **1a**-**3a**, **5a** and **6a**

Parameter	**1a**	**2a**	**3a**·Me_2CO	**5a**	**6a**
Eu-O	2.343(2)-2.369(3)	2.335(4)-2.378(4)	2.347(6)-2.422(6) for Eu1 2.343(6)-2.418(6) for Eu2	2.333(4)-2.384(4)	2.359(5)-2.372(6) for Eu1 2.353(5)-2.369(6) for Eu2
Eu-N	2.598(3), 2.645(3)	2.582(5), 2.591(6)	2.586(7), 2.592(7) for Eu1 2.581(7), 2.596(7) for Eu2	2.562(5), 2.602(5)	2.567(7), 2.584(7) for Eu1 2.578(7), 2.584(6) for Eu2
C-O	1.254(4)-1.271(4)	1.251(8)-1.272(7)	1.255(10)-1.286(10)	1.251(7)-1.272(8)	1.249(9)-1.277(11)
O-Eu-O	71.88(8), 72.19(8), 72.94(9)	71.82(14), 71.88(14), 72.32(15)	70.9(2)-72.1(2)	71.48(15), 71.73(15), 72.60(16)	70.88(19)-71.42(18)
N-Eu-N	62.41(9)	63.31(17)	63.4(2), 63.0(2)	63.08(19)	63.7(2), 63.8(2)

Table S3 Selected Continuous Shape Measures (CShM) values for the potential coordination polyhedra of Eu in the structure of complexes **1a**-**3a**, **5a** and **6a**

Complex	Square antiprism D_{4d}	Triangular dodecahedron D_{2d}	Biaugmented trigonal prism J50 C_{2v}	Biaugmented trigonal prism C_{2v}
1a	1.051	1.318	2.542	1.983
2a	0.703	2.402	2.905	2.2
3a·Me_2CO (Eu1/Eu2)	2.628/2.633	0.578/0.591	3.017/3.059	2.437/2.446
5a	0.585	2.54	2.645	2.205
6a (Eu1/Eu2)	1.929/3.128	0.754/0.381	2.884/3.131	2.373/2.447

Table S4 Selected parameters for π-π interactions in **1a**-**3a**, **5a** and **6a** (C_g-C_g is the distance between the ring centroids (Å); α is the dihedral angle between planes I and J (deg.); C_g(I)-Perp is the perpendicular distance of C_g(I) on ring J (Å); C_g(J)-Perp is the perpendicular distance of C_g(J) on ring I (Å); Slippage is the distance between C_g(I) and perpendicular projection of C_g(J) on ring I (Å))

Complex	Rings I and J	C_g-C_g	α	C_g(I)-Perp	C_g(J)-Perp	Slippage
1a	(N2C30->C34)-(N2C30->C34) [1-x, 2-y, -z]	3.739(2)	0.0(2)	3.419(2)	3.419(2)	1.515
2a	(N1C25->C29)-(N1C25-C29) [1-x, -y, 1-z]	3.668(4)	0.0(3)	3.432(3)	3.432(3)	1.294
3a·Me_2CO	(S5C48-C51)-(N4C66->C70) [x, -1+y, z]	3.896(6)	9.5(5)	3.593(4)	3.349(4)	1.99
	(S5C48->C51)-(C64C65C70C69C72C71) [x, -1+y, z]	3.912(6)	10.5(5)	3.603(4)	3.495(5)	1.756
	(S2C12-C15)-(N4C66-C70) [x, -1+y, z]	3.888(6)	9.4(6)	3.581(5)	3.333(4)	2.002
	(S2C12->C15)-(N4C66->C70) [x, -1+y, z]	3.913(7)	10.7(6)	3.591(5)	3.508(5)	1.733
5a	(N2-C10P->C7P-C12P)-(N2-C10P->C7P-C12P) [1-x, 1-y, 1-z]	3.822(4)	0.0(3)	3.572(3)	3.573(3)	1.358
	(N2-C10P->C7P-C12P)-(C4P->C7P-C12P-C11P) [1-x, 1-y, 1-z]	3.685(4)	4.1(3)	3.542(3)	3.512(3)	1.117
6a	(N1B -C34B-C38B->C35B)-(S4->C4B->C7B)	3.751(5)	7.5(4)	3.385(4)	3.567(3)	1.164
	(S1-C4A->C7A)-(N1A-C34A-C38A->C35A) [x, y, 1+z]	3.869(5)	9.0(4)	3.332(3)	3.598(4)	1.424

Table S5 Selected parameters for C-H...π interactions in **1a**-**3a**, **5a** and **6a** (C_g(J) is the center of gravity of ring J; H-Perp is the perpendicular distance of H to ring plane J (Å); γ is the angle between the C_g-H vector and ring J normal; X-H..C_g is the X-H-C_g angle (deg.); X..C_g is the distance of X to C_g (Å); X-H, Pi is the angle of the X-H bond with the Pi-plane (i.e.' Perpendicular = 90 degrees, Parallel = 0 degrees))

Complex	Elements of C-H...π	H..C_g	H-Perp	γ	X-H..C_g	X..C_g	X-H, Pi
1a	C5-H5...(C28-C29-C34-C33-C36-C35) [1-x, 2-y, 1-z]	2.67	2.56	16.48	136	3.423(4)	58
	C6-H6...(N2C30->C34) [1-x, 2-y, 1-z]	2.91	2.77	18.22	133	3.626(5)	53
	C8-H8C...(S1C4->C7) [1-x, 2-y, 1-z]	2.91	-2.84	12.75	130	3.624(5)	53
	C13-H13...(S1C4->C7) [1-x, 1-y, 1-z]	2.84	2.78	12.16	141	3.626(5)	57
2a	C22-H22...(N1C25-C29) [1-x, -y, -z]	2.91	-2.81	15.41	154	3.790(8)	64
3a·Me_2CO	C32-H32...(S3C20->C23) [x, 1+y, z]	2.61	-2.6	6.76	163	3.533(12)	73
	C78-H78...(S4C40->C43) [x, 1+y, z]	2.62	-2.6	6.48	164	3.542(12)	74
5a	C6B-H6BA...(S1AC4A->C7A) [-1/2+x, 3/2-y, 1-z]	2.97	2.95	6.74	132	3.671(8)	49
	C5P-H5PA...(S1AC4A->C7A) [1-x, 1-y, 1-z]	2.68	-2.66	5.91	147	3.514(9)	52
6a	C16A-H16A...(S4->C4B->C7B) [2-x, -y, 1-z]	2.63	2.61	7.80	149	3.480(9)	58
	C27'-H27B...(S1-C4A->C7A) [1-x, -y, 1-z]	2.62	-2.62	2.89	152	3.489(19)	59
	C39B-H39B...(S5-C15B->C18B) [1-x, -y, 1-z]	2.61	-2.59	8.13	158	3.513(10)	68
	C19A-F10A...2 [2-x, -y, 1-z]	3.962(7)	3.520	27.32	86.3(5)	4.102(9)	1.93
	C33X-F26X...3 [1-x, -y, -z]	3.64(2)		20.79	119.5(14)	4.458(18)	12.40
	C20A-F12A...(N2A-C44A->C41A-C45A)	3.182(9)	3.095	13.52	158.8(6)	4.522(13)	60.20
	C20B-F12B...(N2B-C44B->C41B-C45B)	3.162(8)	3.135	7.69	124.2(6)	4.107(13)	37.70
	C31A-F20A...(N1A-C34A-C38A->C35A)	3.575(9)	-3.513	10.68	124.4(6)	4.467(10)	25.14
	C31A-F21A...(C34A-C38A->C41A-C45A)	3.233(8)	-3.100	16.50	131.0(6)	4.284(11)	45.69
	C32B-F24B...(N2B-C44B->C41B-C45B)	3.110(13)	-3.025	13.38	128.0(9)	4.075(12)	38.30

Table S6 Selected parameters for the C-H...O, C-H...S and C-H...F intermolecular interactions in **1a**-**3a**, **5a** and **6a**

Complex	D-H...A	D-H, Å	H...A, Å	D...A, Å	D-H...A, deg.
1a	C26-H26...O4 [-1+x, y, z]	0.95	2.41	3.297(5)	156
	C27-H27...O2 [-1+x, y, z]	0.95	2.58	3.428(5)	148
	C30-H30...O6	0.95	2.53	3.136(5)	122
2a	C30-H30...O3	0.95	2.55	3.218(8)	128
	C32-H32...O6 [1+x, y, z]	0.95	2.48	3.353(8)	153
3a·Me_2CO	C5-H5A...O1S [2-x, -1/2+y, 1-z]	0.95	2.58	3.498(14)	163
	CC27-H27...O2 [-1+x ,y, z]	0.95	2.57	3.328(13)	136
	C57-H57...O2S [2-x, -1/2+y, -z]	0.95	2.57	3.493(14)	164
	C63-H63...O12 [-1+x ,y, z]	0.95	2.56	3.347(12)	140
	C78-H78...S4A [x, 1+y, z]	0.95	2.82	3.60(3)	140
5a	C6A-H6AA...O1 [-x+3/2, y-1/2, z]	0.95	2.51	3.220	131.3
	C7A-H7AA...F5Z [-x+3/2, -y+1, z-1/2]	0.95	2.38	3.233	149.1
	C6-H6A...F6 [x, -y+3/2, z-1/2]	0.95	2.28	3.051	137.2
	C2P-H2PA...F5 [x-1/2, y, -z+3/2]	0.95	1.88	2.619	133.3
	C9P-H9PA...F5B [x, -y+3/2, z-1/2]	0.95	2.53	3.257	133.5
6a	C5A-H5AA...F24B [x, y, z+1]	0.95	2.42	3.318	157.4
	C16A-H16A...S4 [-x+2, -y, -z+1]	0.95	2.88	3.778	157.7
	C17A-H17A...F17A [-x+2, -y, -z+1]	0.95	2.58	3.254	128.1
	C27A-H27A...O1B [-x+1, -y, -z+1]	0.95	2.50	3.137	123.8
	C29A-H29A...F6A [x, y-1, z]	0.95	2.59	3.534	174.6
	C35A-H35A...O5A	0.95	2.62	3.103	112.0
	C36A-H36A...F20A [-x+1, -y, -z+1]	0.95	2.49	3.427	167.4
	C43A-H43A...F21A [-x+1, -y+1, -z+1]	0.95	2.48	3.406	164.1
	C44A-H44A...O2A	0.95	2.50	3.139	125.1
	C16B-H16B...O1A [-x+1, -y, -z+1]	0.95	2.49	3.143	126.2
	C27'-H27B...S1 [-x+1, -y, -z+1]	0.95	3.01	3.833	145.4
	C28-H28B...F27X [-x+1, -y, -z]	0.95	2.02	2.796	137.9
	C29'-H29B...F6B [x, y-1, z]	0.95	2.56	3.352	140.5
	C35B-H35B...O5B	0.95	2.63	3.115	112.2
	C36B-H36B...F13B [-x+2, -y, -z]	0.95	2.63	3.399	138.0
	C44B-H44B...O2B	0.95	2.49	3.160	128.0

Table S7 Selected parameters for the S...F and C-F...F-C intermolecular interactions in **2a**, **3a**, **5a** and **6a**

Complex	Type of interactions	*d*, Å
2a	S1...F1 [1+x, y, z]	3.342(5)
3a·Me_2CO	S2...F6 [-1+x,y,z]	2.960(9)
	F1...F4 [x,1+y,z]	2.927(12)
	F6...S2 [1+x,y,z]	2.960(9)
5a	S1... F7A [x, 3/2-y, -1/2+z]	3.227(10)
	S1B...F1 [-1/2+x, 3/2-y, 1-z]	3.164(6)
	F1... S1B [1/2+x, 3/2-y, 1-z]	3.164(6)
	F1A...F2B [1-x, -1/2+y, 3/2-z]	2.963(7)
	F1A...F5H [1-x, -1/2+y, 3/2-z]	2.956(13)
	F1B...F7' [-1/2+x, y, 3/2-z]	2.973(19)
	F2B... F1A [1-x, 1/2+y, 3/2-z]	2.963(7)
6a	F1B... F25X [1-x, 1-y, -z]	2.71(3)
	F2B...F17'	2.866(11)
	F6B...F25X [1-x, 1-y, -z]	2.67(3)
	F16B...F16B [2-x, -y, 1-z]	2.721(17)
	F18B...F24X [1+x, y, z]	2.73(2)
	F26B... F1A' [x, y, -1+z]	2.69(2)
	F9A...F26A [1-x, 1-y, 1-z]	2.897(16)
	F22A...F15F [1-x, 1-y, -z]	2.841(13)
	F26A...F16' [-1+x, y, z]	2.763(15)
	F17A...F3B	2.63(3)

Table S8 Spherical atomic coordinates for the coordination polyhedra of **1a**-**10a**

Complex	Atom	R, Å	θ, °	ϕ, °	Complex	Atom	R, Å	θ, °	ϕ, °
1a	N	2.5229	96.00	170.29	**6a**	N	2.4988	143.18	281.70
	N	2.5173	109.11	103.56		N	2.5076	149.19	82.96
	O	2.3734	19.17	164.7		O	2.3799	9.91	169.17
	O	2.3749	56.14	49.45		O	2.3974	67.82	86.24
	O	2.3729	82.68	250.57		O	2.3774	69.41	312.97
	O	2.3773	70.50	318.96		O	2.4008	94.16	14.85
	O	2.3731	159.76	242.11		O	2.3768	83.76	224.95
	O	2.3780	128.81	13.71		O	2.4005	100.61	161.28
2a	N	2.5117	62.88	283.27	**7a**	N	2.5112	140.00	253.72
	N	2.5117	84.89	349.32		N	2.4979	140.34	135.63
	O	2.3763	25.00	69.28		O	2.3993	117.76	353.61
	O	2.3836	52.05	184.88		O	2.3774	96.43	59.35
	O	2.3766	102.50	69.11		O	2.3996	76.00	209.55
	O	2.3880	114.67	139.52		O	2.3764	61.60	140.05
	O	2.3737	161.81	322.44		O	2.3937	65.93	290.93
	O	2.3960	116.04	230.94		O	2.3796	25.63	16.82
3a	N	2.5069	111.14	100.85	**8a**	N	2.5111	137.61	258.59
	N	2.5055	93.58	167.06		N	2.4977	141.33	143.28
	O	2.3991	78.40	318.82		O	2.3997	118.30	356.87
	O	2.3720	18.54	125.39		O	2.3773	99.03	63.92
	O	2.4036	65.83	40.21		O	2.3995	74.01	214.27
	O	2.4011	142.25	11.47		O	2.3767	62.80	143.96
	O	2.3734	142.77	246.10		O	2.3937	63.92	296.25
	O	2.3784	65.70	248.78		O	2.3785	27.03	25.57
4a	N	2.5067	147.35	246.42	**9a**	N	2.5071	133.11	257.29
	N	2.5006	141.51	104.93		N	2.4998	148.14	138.83
	O	2.4047	116.16	351.10		O	2.4014	119.83	356.02
	O	2.3728	77.60	45.61		O	2.3767	95.26	60.77
	O	2.3994	82.03	200.38		O	2.3991	69.58	213.16
	O	2.3756	69.64	133.38		O	2.3748	72.04	143.25
	O	2.3912	74.55	287.54		O	2.3948	64.40	304.05
	O	2.3824	8.76	314.67		O	2.3802	19.99	36.51
5a	N	2.5041	76.81	201.25	**10a**	N	2.5068	128.06	252.87
	N	2.5049	140.91	222.09		N	2.4999	148.25	144.93
	O	2.3719	94.20	301.25		O	2.4023	123.65	351.26
	O	2.4019	30.82	281.14		O	2.3756	99.53	58.16
	O	2.3735	134.29	22.06		O	2.3993	64.54	209.60
	O	2.4032	67.43	24.97		O	2.3751	72.37	138.79
	O	2.3717	114.00	116.00		O	2.3938	63.41	304.86
	O	2.4043	48.71	117.38		O	2.3809	24.07	37.30

Table S9 Energy of the $^5D_0 \rightarrow {}^7F_0$ transition and energy of the LMCT state of compounds **1a**-**10a**

Complex	E_{00}, cm^{-1}	E_{LMCT}, cm^{-1}
1a	17211	23104
2a	17204	22870
3a	17205	22934
4a	17196	22726
5a	17202	22841
6a	17196	22855
7a	17195	22952
8a	17193	22865
9a	17188	22914
10a	17188	22725

Table S10 Experimental and theoretical (calculated using the crystallographic structure and the RM1 method) Judd-Ofelt parameters (Ω_λ, $\lambda = 2,4,6$)

Complex		Ω_2, 10^{-20} cm^2	Ω_4, 10^{-20} cm^2	Ω_6, 10^{-20} cm^2
	exp	38.40	4.33	—
1a	crystal	38.31	4.92	0.9261
	RM1	38.22	5.28	1.2145
	exp	24.75	7.33	—
2a	crystal	24.17	8.63	1.5332
	RM1	24.71	7.42	0.3944
	exp	22.99	7.34	—
3a	crystal	22.98	7.34	0.2048
	RM1	23.00	7.53	0.2337
	exp	22.33	6.73	—
4a	crystal	—	—	—
	RM1	22.26	6.91	0.5377
	exp	25.93	7.23	—
5a	crystal	25.93	7.23	0.1397
	RM1	25.73	7.63	0.8781
	exp	24.58	5.59	—
6a	crystal	24.57	5.64	0.2333
	RM1	24.57	5.59	0.1602
	exp	23.47	5.28	—
7a	crystal	—	—	—
	RM1	23.20	6.01	1.0827
	exp	25.23	6.86	—
8a	crystal	—	—	—
	RM1	24.99	7.44	1.0032
	exp	28.38	6.31	—
9a	crystal	—	—	—
	RM1	28.05	7.68	1.2004
	exp	27.75	6.20	—
10a	crystal	—	—	—
	RM1	27.31	7.40	1.5297