Supplementary materials

Cerium(III) complexes with azolyl-substituted thiophenolate ligands: synthesis, structure and red luminescence

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Table 1S. Details of crystallographic, collection and refinement data for **Ce(SSN)$_3$(DME)**, **Ce(NSN)$_3$(DME)**, **La(OSN)$_3$(DME)**.

Complex	**Ce(SSN)$_3$(DME)**	**Ce(NSN)$_3$(DME)**	**La(OSN)$_3$(DME)**
Empirical formula	$C_{45}H_{39}CeN_3O_3S_6$	$C_{48}H_{49.50}CeN_6O_{4.50}S_3$	$C_{43}H_{34}LaN_3O_5S_3$
Formula weight	1002.27	1018.73	907.82
Temperature [K]	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	Pbca	I2/a	P-1
Unit cell dimensions			
a[Å]	15.0364(5)	21.5274(3)	11.2387(13)
b[Å]	21.7390(8)	12.4640(2)	12.7989(13)
c[Å]	25.9182(9)	39.1836(5)	13.7827(12)
α[°]	90	90	88.854(8)
β[°]	90	95.4840(10)	81.032(8)
γ[°]	90	90	72.201(10)
Volume [Å^3]	8472.0(5)	10465.5(3)	1863.8(3)
Z	8	8	2
Calculated density [Mg/m^3]	1.572	1.293	1.618
Absorption coefficient [mm^{-1}]	1.415	1.035	1.366
F(000)	4064	4172	916
Crystal size [mm^3]	0.35×0.15×0.13	0.43×0.27×0.18	0.15×0.10×0.03
θ [°]	1.874 - 27.869	3.081 - 28.306	3.110 - 25.115
Reflections collected / unique	81561 / 10099	55315 / 12956	25645 / 6601
R(int)	0.0671	0.0467	0.1158
Final R indices [I>2sigma(I)]	R_1=0.0374, wR_2=0.0851	R_1=0.0577, wR_2=0.1658	R_1=0.0515, wR_2=0.0969
R indices (all data)	R_1=0.0549, wR_2=0.0939	R_1=0.0770, wR_2=0.1826	R_1=0.0909, wR_2=0.1104
S	1.081	1.030	1.019
Largest diff. peak and hole [e/Å^3]	1.563/-0.575	1.886/-1.645	1.095/-0.859

Table 2S. The selected bond lengths (Å) and angles (°) in the **Ce(SSN)$_3$(DME)**, **Ce(NSN)$_3$(DME)** and **La(OSN)$_3$(DME)** complexes.

Bond	**Ce(SSN)$_3$(DME)**, Å	Bond	**Ce(NSN)$_3$(DME)**, Å	Bond	**La(OSN)$_3$(DME)**, Å
Ce(1)-S(1)	2.8588(8)	Ce(1)-S(1)	2.8792(12)	La(1)-S(1)	2.8679(18)
Ce(1)-S(3)	2.8839(8)	Ce(1)-S(2)	2.8874(12)	La(1)-S(2)	2.8666(17)
Ce(1)-S(5)	2.8714(8)	Ce(1)-S(3)	2.9330(11)	La(1)-S(3)	2.8598(15)
Ce(1)-N(1)	2.891(3)	Ce(1)-N(1)	2.729(4)	La(1)-N(1)	2.739(5)
Ce(1)-N(2)	2.620(2)	Ce(1)-N(3)	2.549(4)	La(1)-N(2)	2.663(5)
Ce(1)-N(3)	2.699(2)	Ce(1)-N(5)	2.643(3)	La(1)-N(3)	2.713(5)
Ce(1)-O(1)	2.568(2)	Ce(1)-O(1)	2.577(3)	La(1)-O(4)	2.630(4)
Ce(1)-O(2)	2.661(2)	Ce(1)-O(2)	2.649(3)	La(1)-O(5)	2.655(4)
Angle	**Ce(SSN)$_3$(DME)**, °	Angle	**Ce(NSN)$_3$(DME)**, °	Angle	**La(OSN)$_3$(DME)**, °
N(1)-Ce(1)-S(1)	70.64(5)	N(1)-Ce(1)-S(1)	70.59(9)	N(1)-La(1)-S(1)	68.56(11)
N(2)-Ce(1)-S(3)	71.15(6)	N(3)-Ce(1)-S(2)	73.85(9)	N(2)-La(1)-S(2)	70.03(11)
N(3)-Ce(1)-S(5)	71.64(6)	N(5)-Ce(1)-S(3)	71.69(8)	N(3)-La(1)-S(3)	69.66(11)

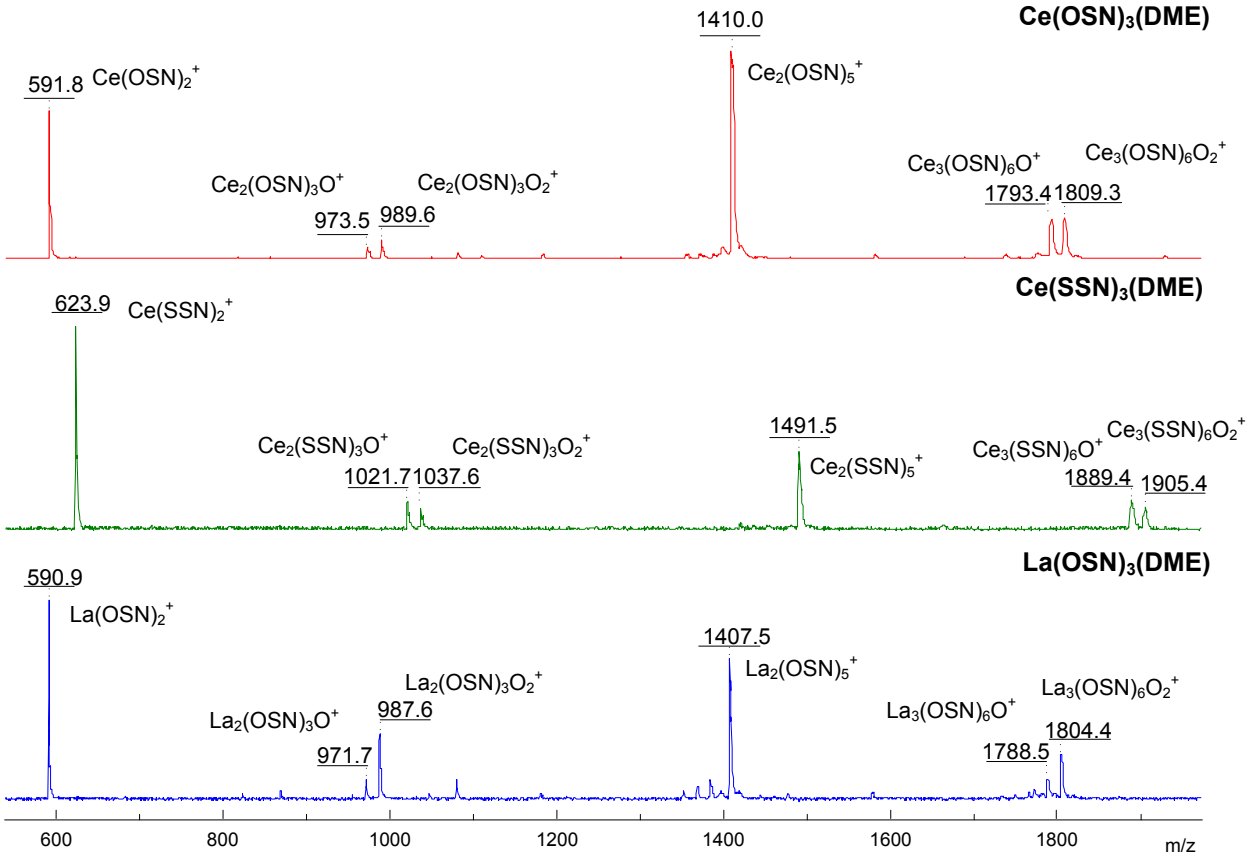

Figure 1Sa. MALDI mass spectra of complexes of **Ce(OSN)$_3$(DME)**, **Ce(SSN)$_3$(DME)**, **La(OSN)$_3$(DME)** recorded in positive mode.

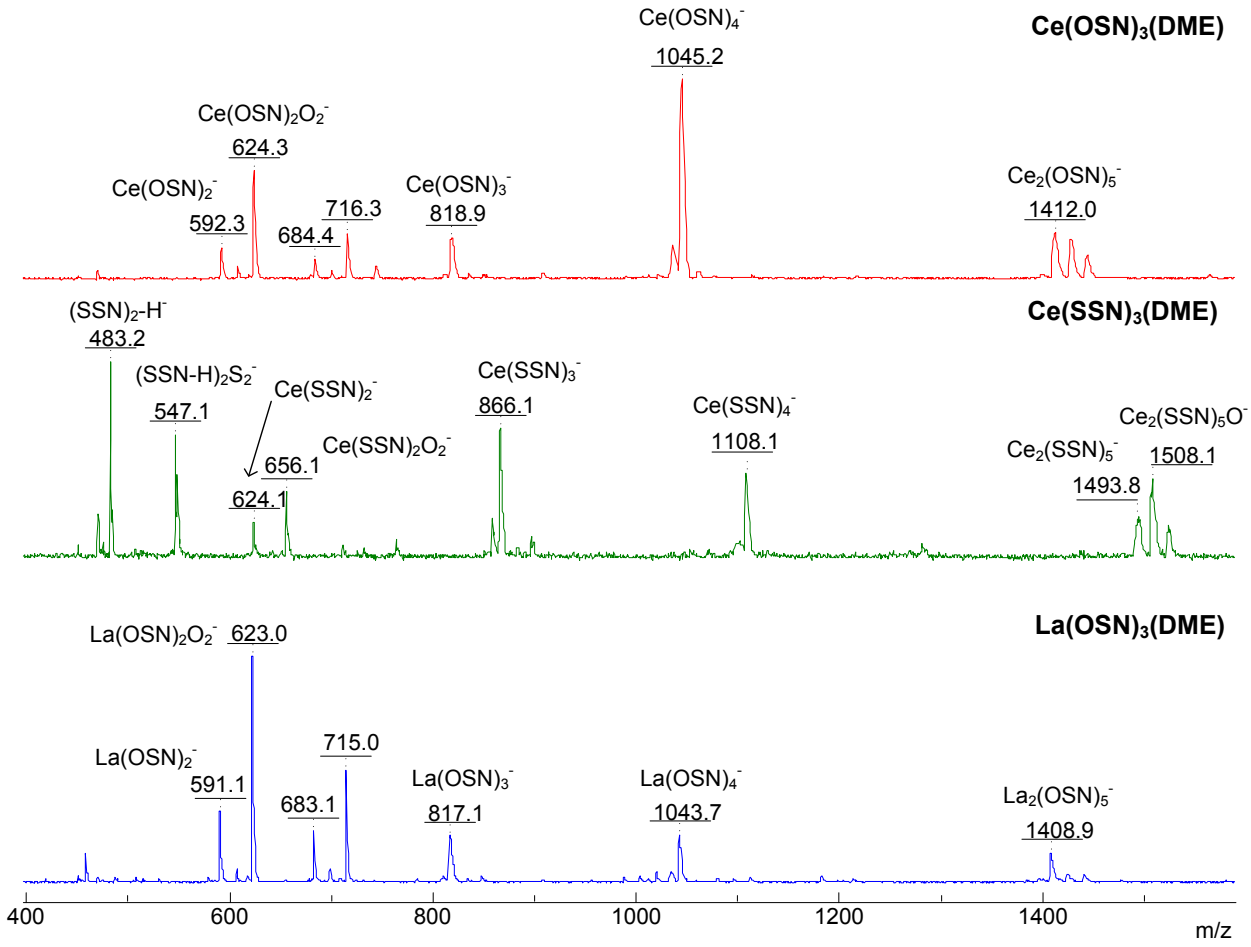

Figure 1Sb. MALDI mass spectra of complexes of **Ce(OSN)$_3$(DME)**, **Ce(SSN)$_3$(DME)**, **La(OSN)$_3$(DME)** recorded in negative mode.

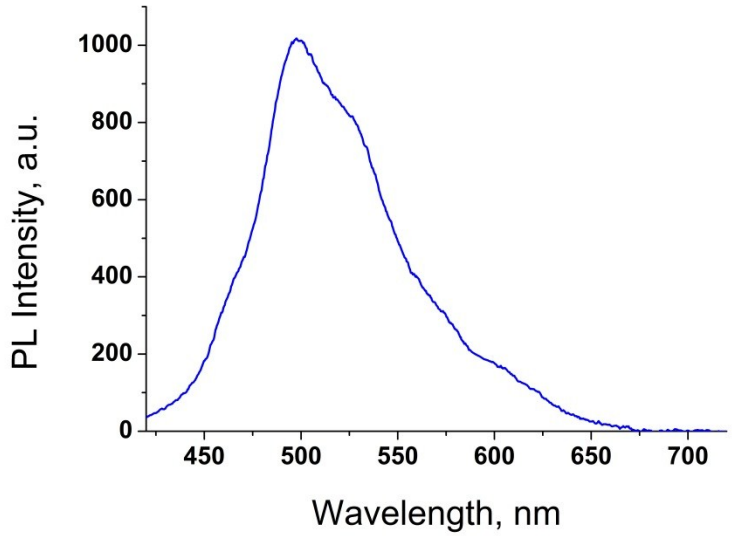

Figure 2S. PL spectrum of **La(OSN)$_3$(DME)** in solid state. Excitation – 405 nm laser diode.

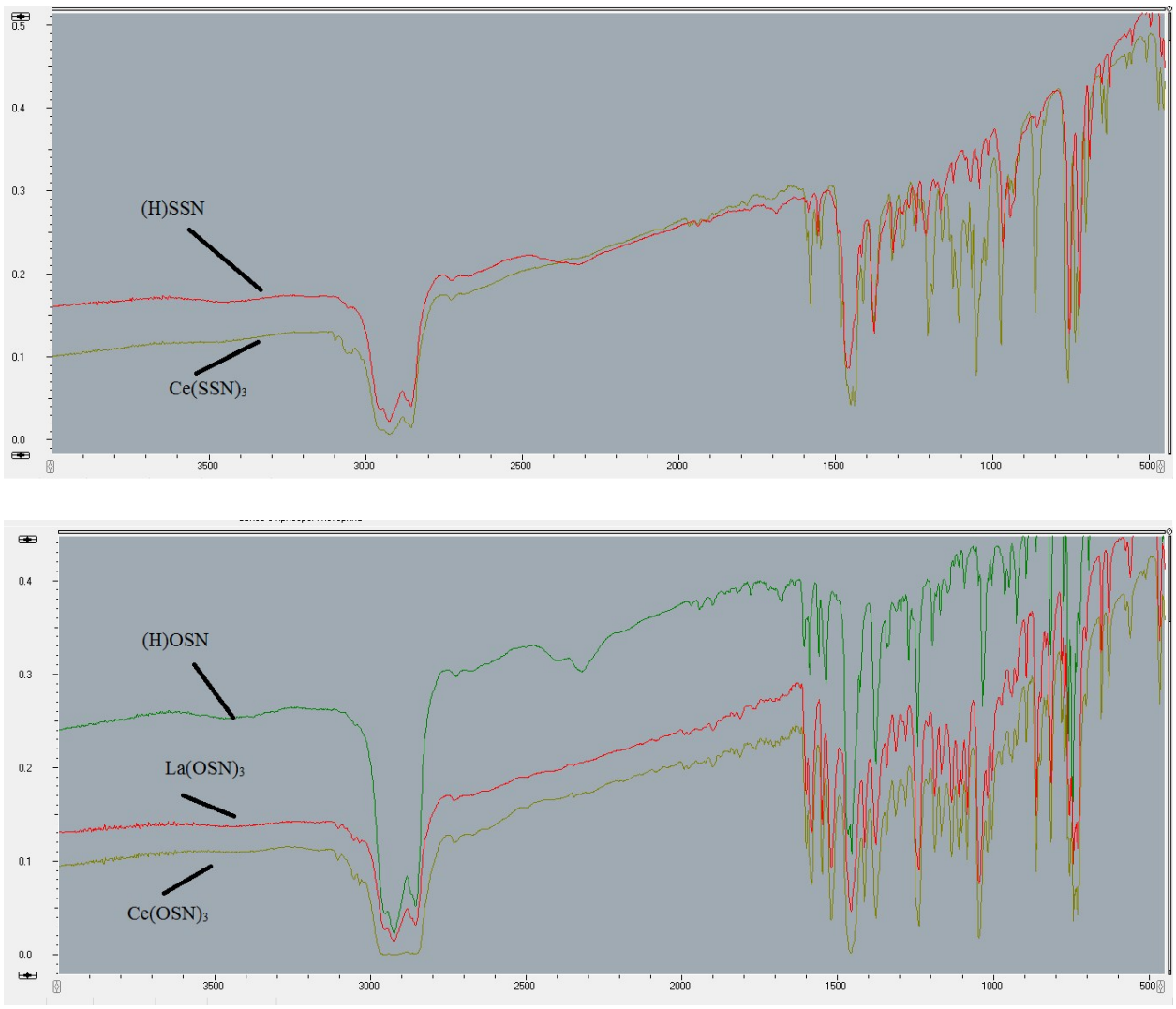

Figure 3S. IR spectra of **(H)OSN**, **(H)SSN**, **La(OSN)3DME**, **Ce(OSN)3DME** and **Ce(SSN)3DME**