

卤代芳香族羧酸与含氮配体合成镧系配合物的结构、热化学和荧光性质

王晨璐¹, 宿素玲², 任宁^{3,*}, 张建军^{1,*}

¹河北师范大学分析测试中心, 化学与材料科学学院, 石家庄 050024

²河北省特种设备监督检验研究院, 石家庄 050000

³邯郸学院, 化学化工与材料学院, 河北省杂环化合物重点实验室, 河北 邯郸 056005

Construction, Thermochemistry, and Fluorescence Properties of Novel Lanthanide Complexes Synthesized from Halogenated Aromatic Carboxylic Acids and Nitrogen-Containing Ligands

Chenlu Wang ¹, Suling Xu ², Ning Ren ^{3,*}, Jianjun Zhang ^{1,*}

¹ Testing and Analysis Center, College of Chemistry & Material Science, Hebei Normal University, Shijiazhuang 050024, China.

² Hebei Special Equipment Supervision and Inspection Institute, Shijiazhuang 050000, China.

³ College of Chemical Engineering & Material, Hebei Key Laboratory of Heterocyclic Compounds, Handan University, Handan 056005, Hebei Province, China.

*Corresponding authors. Emails: jjzhang6@126.com (Z.J.); ningren9@163.com (R.N.); Tel.: +86-311-80786457 (Z.J.); +86-310-6260302 (R.N.)

Table S1 Reagents required for the experiment.

Materials	Source	Purity	CAS number
1,10-phenanthroline	China·Beijing Innochem	97%	66-71-7
2,4-difluorobenzoic acid	China·Beijing Innochem	98%	1583-58-0
2,2':6'2"-tripyrindine	China·Ark Pharm	97%	1148-79-4
2-chloro-6-fluorobenzoic acid	China·Beijing Innochem	98%	434-75-3
Sm(NO ₃) ₃ ·6H ₂ O	China·Alfa Aesar	99.90%	13759-83-6
Eu(NO ₃) ₃ ·6H ₂ O	China·Beijing Innochem	99.99%	10031-53-5
Er(NO ₃) ₃ ·5H ₂ O	China·Damas-beta	99%+	10031-51-3
Tb(NO ₃) ₃ ·6H ₂ O	China·Beijing Innochem	99.90%	57584-27-7
Dy(NO ₃) ₃ ·5H ₂ O	China·Alfa Aesar	99.90%	10031-49-9
NaOH	China·Tianjin Senchang	96%	1310-73-2
C ₂ H ₅ OH	China·Damao chemical	AR	64-17-5

Table S2 Primary bond lengths of the complexes 1-5.

Complex 1		Complex 2		Complex 3		Complex 4		Complex 5	
Select bond	Bond length/Å	Select bond	Bond length/Å	Select bond	Bond length/Å	Select bond	Bond length/Å	Select bond	Bond length/Å
Sm(1)—O(3)	2.312(6)	Eu(1)—O(3)	2.299(5)	Er(1)—O(3)	2.286(6)	Tb(1)—O(2)#1	2.303(4)	Dy(1)—O(2)#1	2.302(4)
Sm(1)—O(4)	2.369(6)	Eu(1)—O(4)	2.354(5)	Er(1)—O(4)	2.335(6)	Tb(1)—O(3)	2.312(4)	Dy(1)—O(3)	2.323(4)
Sm(1)—O(1)	2.393(6)	Eu(1)—O(1)	2.370(5)	Er(1)—O(1)	2.299(6)	Tb(1)—O(1)	2.366(4)	Dy(1)—O(1)	2.369(4)
Sm(1)—O(5)	2.469(6)	Eu(1)—O(5)	2.454(5)	Er(1)—O(2)	2.243(6)	Tb(1)—O(8)	2.417(4)	Dy(1)—O(8)	2.426(4)
Sm(1)—O(2)	2.425(5)	Eu(1)—O(2)	2.393(5)	Er(1)—O(6)	2.376(6)	Tb(1)—N(1)	2.512(5)	Dy(1)—N(1)	2.520(5)
Sm(1)—O(6)	2.469(6)	Eu(1)—O(6)	2.466(5)	Er(1)—O(5)	2.422(6)	Tb(1)—N(3)	2.544(5)	Dy(1)—N(3)	2.539(5)
Sm(1)—N(2)	2.586(7)	Eu(1)—N(2)	2.575(6)	Er(1)—N(2)	2.502(7)	Tb(1)—O(5)	2.527(4)	Dy(1)—O(5)	2.543(4)
Sm(1)—N(1)	2.632(7)	Eu(1)—N(1)	2.589(6)	Er(1)—N(1)	2.537(7)	Tb(1)—N(2)	2.567(5)	Dy(1)—N(2)	2.583(4)
Sm(1)—O(1)#1	2.882(6)	Eu(1)—O(1)#1	2.870(5)			Tb(1)—O(6)	2.509(4)	Dy(1)—O(6)	2.521(4)

Equivalent atoms generated by symmetry transformations: #1 -x + 1, -y + 1, -z + 1.

Table S3 Infrared spectral data of ligands and complexes 1-5.

Ligand/Complex	$\nu_{C=N}$	δ_{C-H}	$\nu_{C=O}$	$\nu_{as(coo-)}$	$\nu_{s(coo-)}$	ν_{Ln-O}
2,4-DFHBA			1691			
phen	1560	854,738				
1	1591	849,729		1639	1429	416
2	1589	849,731		1626	1429	419
3	1593	850,731		1639	1431	419
2-Cl-6-FHBA			1703			
terpy	1561	762,656				
4	1578	769,652		1636	1454	426
5	1583	775,652		1605	1449	426

Table S4 Raman spectral data of ligands and complexes 1-5.

Ligand/Complex	$\nu_{C=N}$	δ_{C-H}	$\nu_{C=O}$	$\nu_{as(coo-)}$	$\nu_{s(coo-)}$	ν_{Ln-O}	ν_{Ln-N}
2,4-DFHBA			1634				
phen	1507	719					
1	1516	724		1611	1417	418	246
2	1520	726		1609	1410	415	241
3	1521	724		1606	1417	420	244
2-Cl-6-FHBA			1652				
terpy	1575	834					
4	1573	733		1601	1501	489	213
5	1572	725		1601	1501	490	213

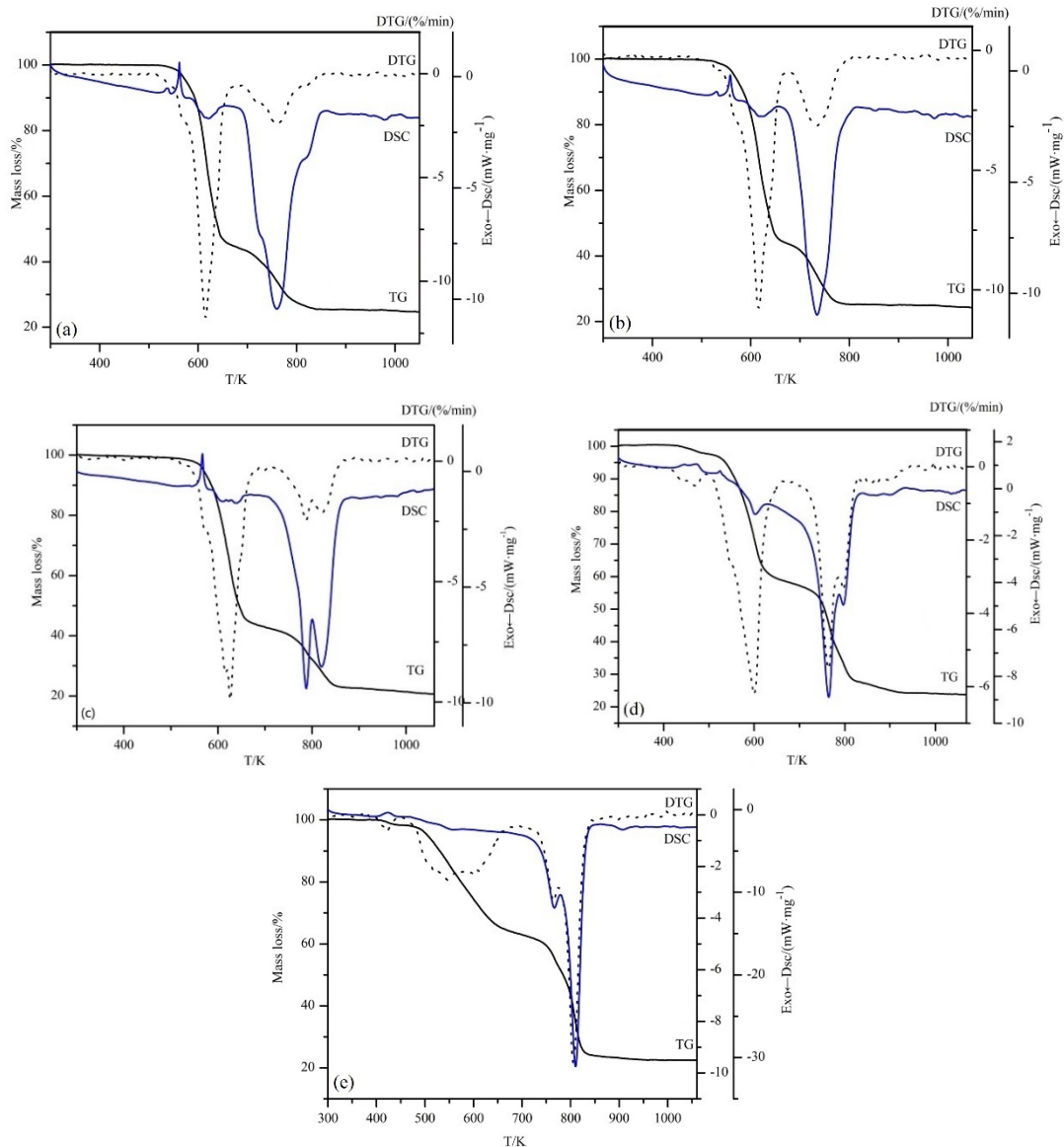


Fig. S1 (a-e) Thermal decomposition curves of complexes 1-5 (complexes 1-5 correspond to a-e, respectively).

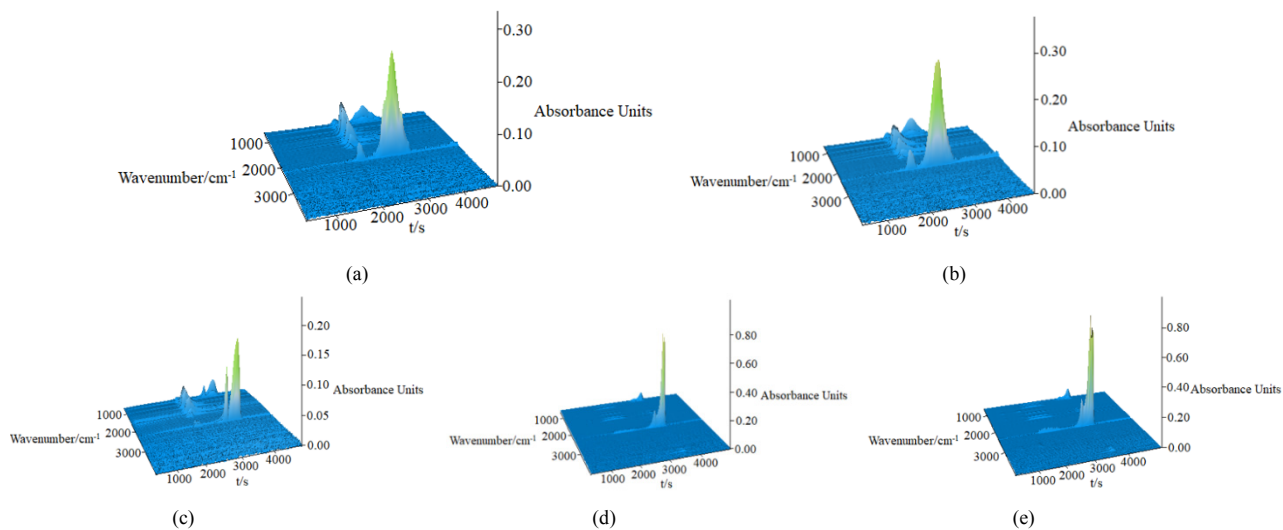


Fig. S2 (a-e) Three-dimensional infrared fugitive gas stacking of complexes 1-5 (complexes 1-5 correspond to a-e, respectively).

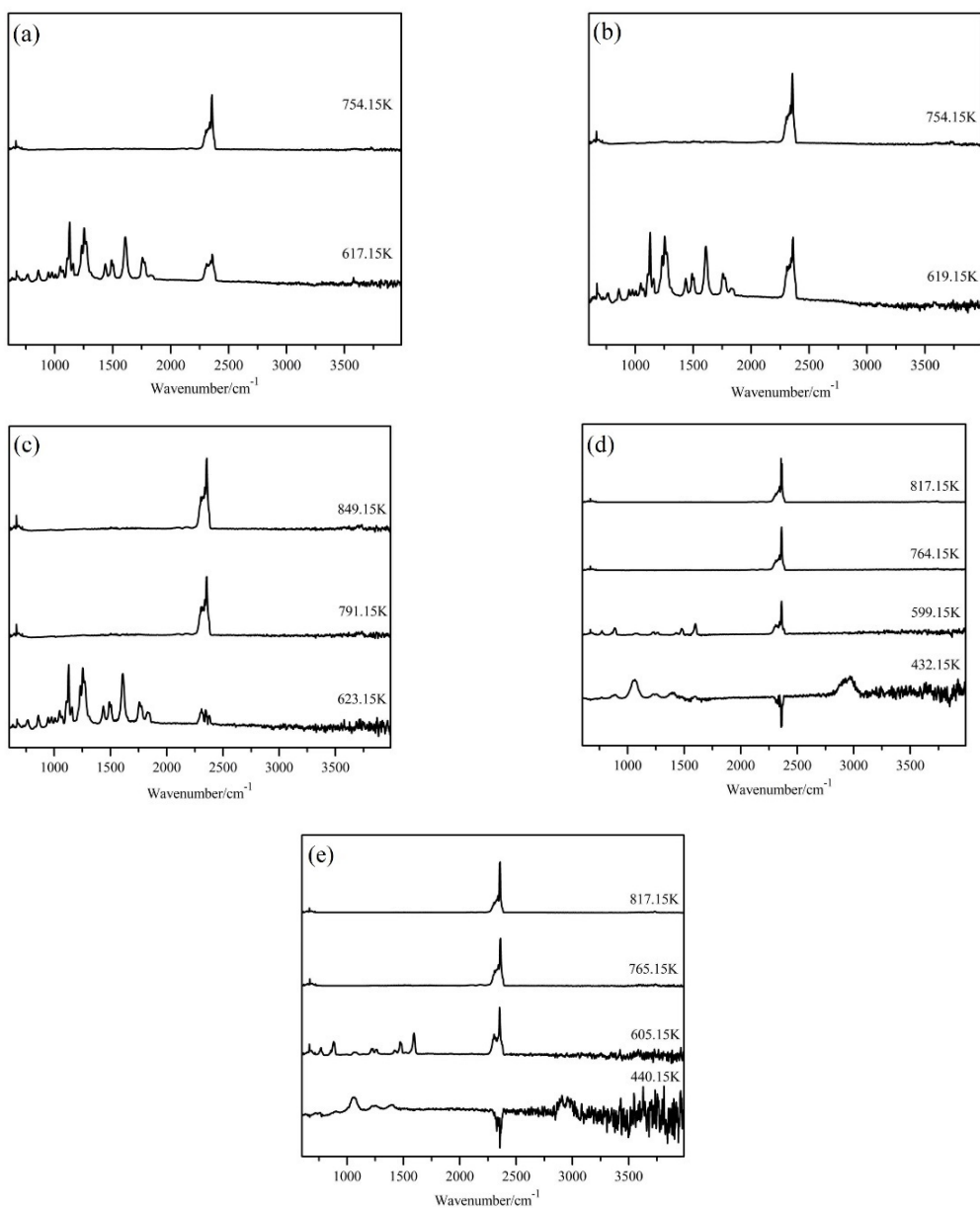


Fig. S3 (a-e) The strongest IR signal peaks of the escaping gases of complexes 1-5 (complexes 1-5 correspond to a-e, respectively).