Electronic Supplementary Information

Chiral Lanthanide-Silver(I) Cluster-based Metal-Organic Frameworks Exhibiting Solvent Stability, and Tunable Photoluminescence

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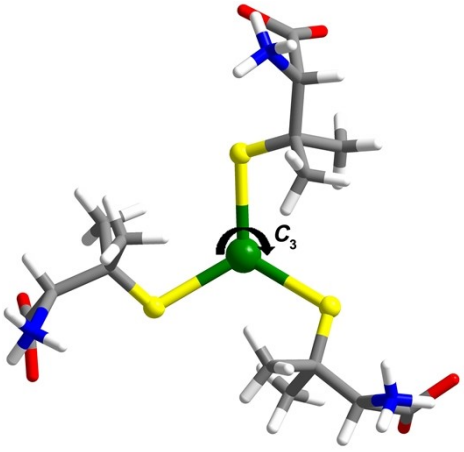

Fig. S1 Ag(I)-centered triangular complex {Ag(*L*-HL)$_3$} featuring C_3 symmetry in **1-*L***.

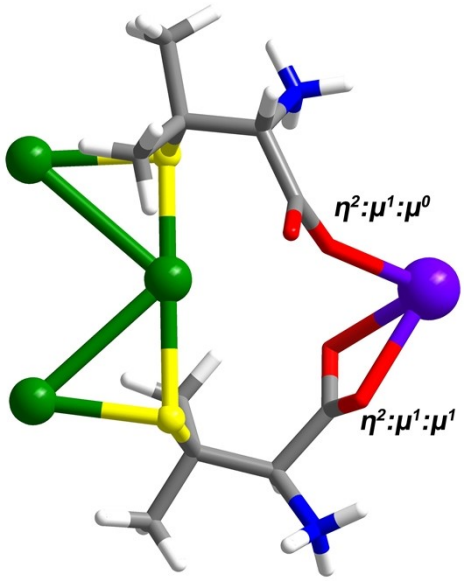

Fig. S2 Two kinds of coordination modes between Gd^{3+} and *L*-HL^- ligand in **1-*L***.

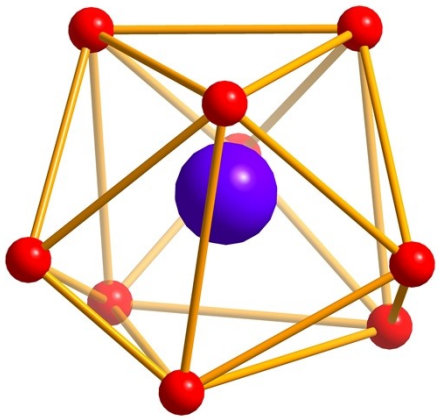

Fig. S3 Two kinds of coordination modes between Gd^{3+} and *L*-HL^- ligand in **1-*L***.

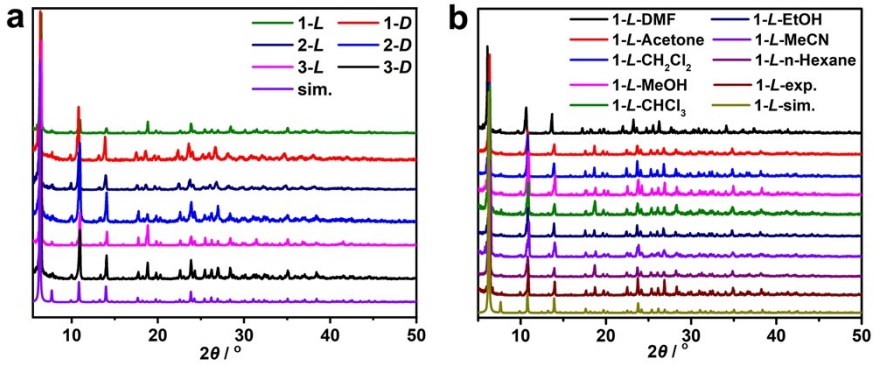

Fig. S4 (a) The experimental and simulated PXRD spectra of ***L*-LnAg5-3D** and ***D*-LnAg5-3D**; (b) the PXRD of compound **1-*L*** before and after immersion in different polar organic solvents.

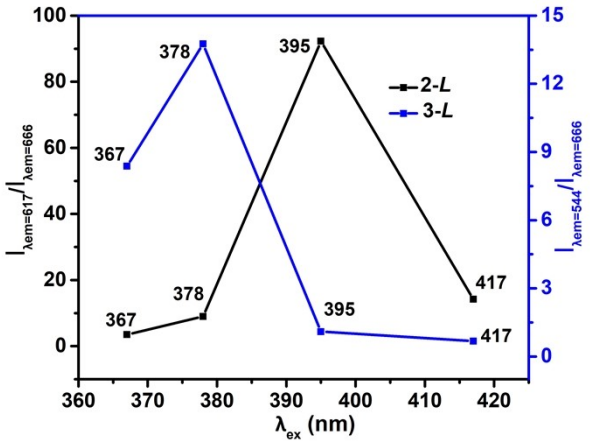

Fig. S5 The ratio of the emission intensity of Ln^{3+} (λ_{em} = 617 nm for Eu^{3+}, λ_{em} =544 nm for Tb^{3+}) to that of $\{Ag_5S_6\}$ moiety (λ_{em} = 666 nm) varied with the excitation wavelengths in compounds **2-*L*** and **3-*L***.

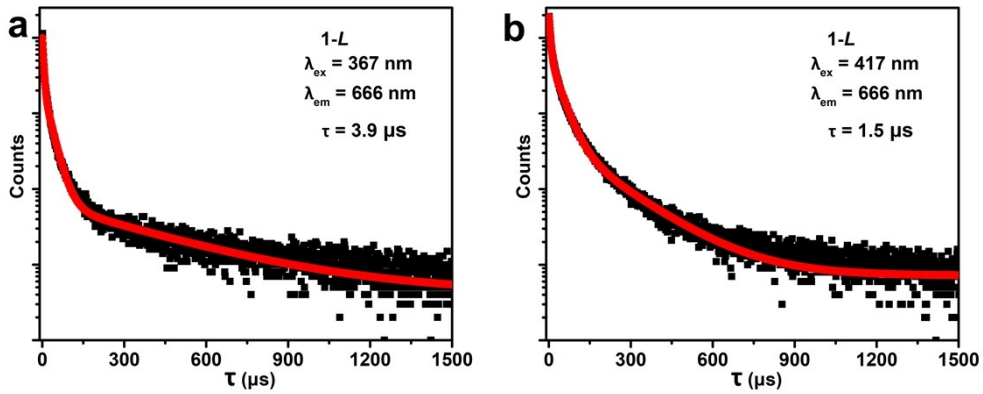

Fig. S6 (a, b) The decay curves of compound **1-*L*** at λ_{ex} = 367/417 nm, λ_{em} = 666 nm.

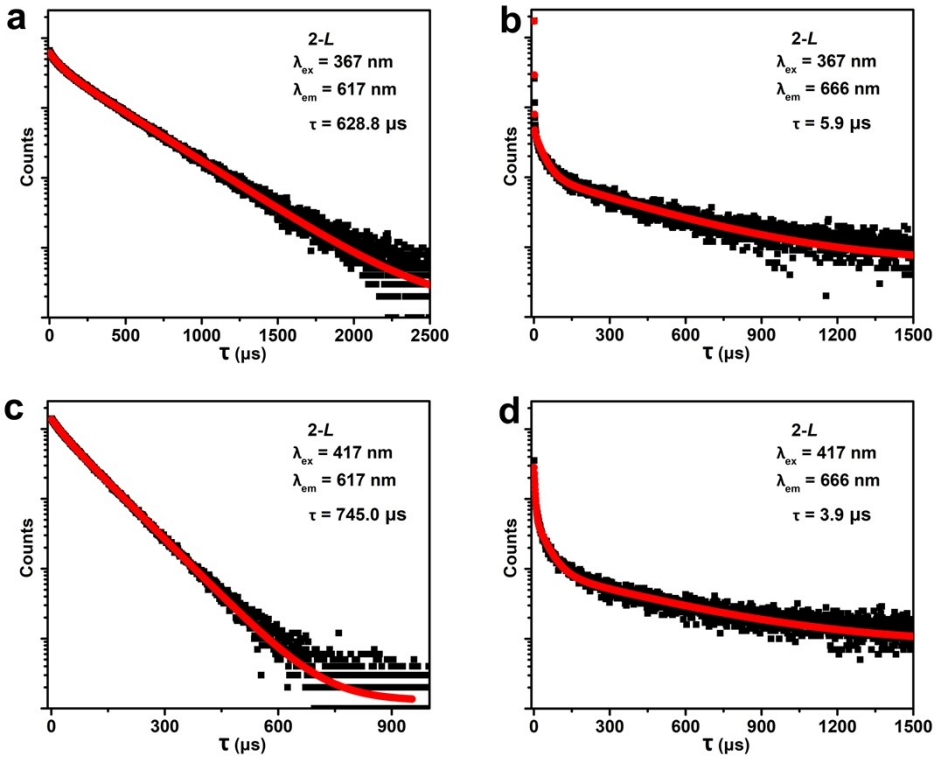

Fig. S7 The decay curves of compound **2-*L*** at λ_{ex} = 367 nm, λ_{em} = 617/666 nm (a, b) and λ_{ex} = 417 nm, λ_{em} = 617/666 nm (c, d).

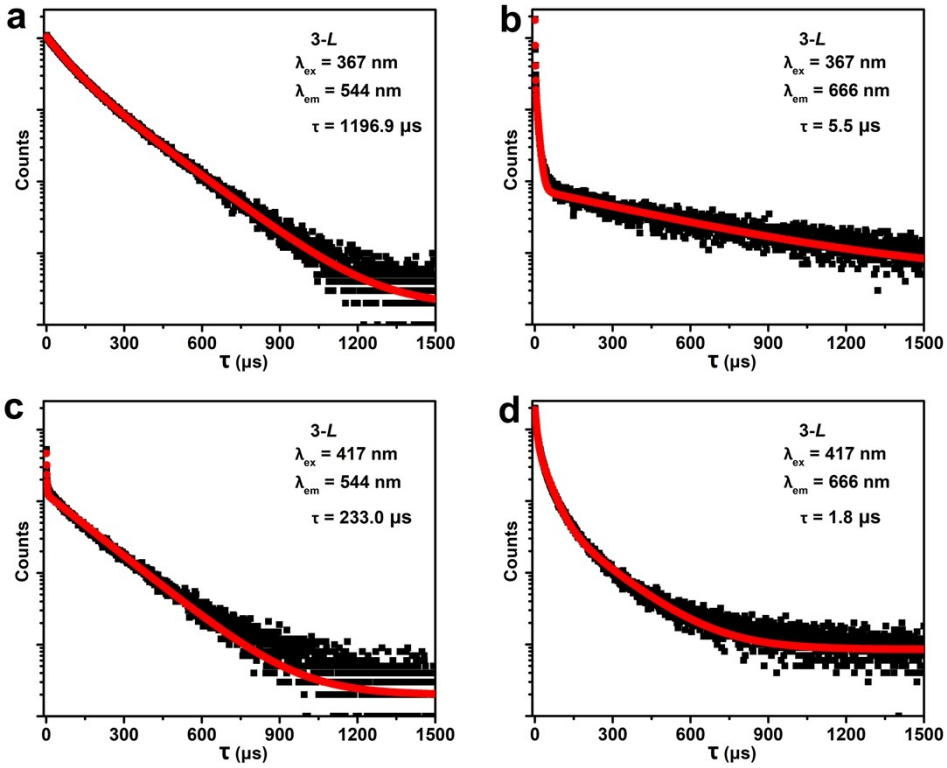

Fig. S8 The decay curves of compound **3-*L*** at λ_{ex} = 367 nm, λ_{em} = 544/666 nm (a, b) and λ_{ex} = 417 nm, λ_{em} = 544/666 nm (c, d).

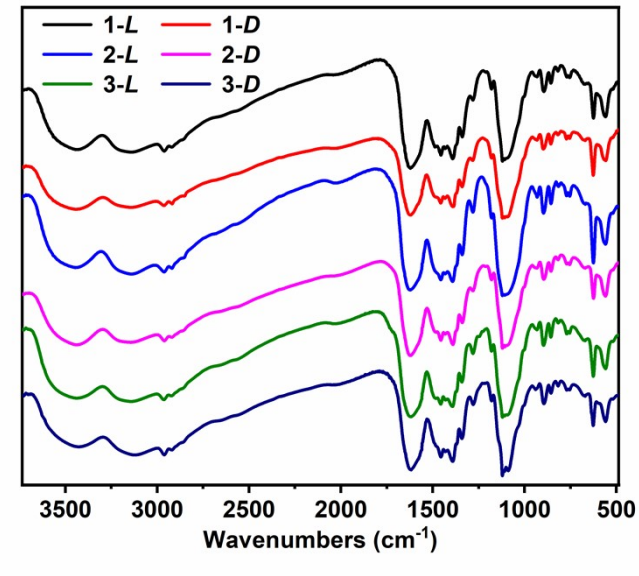

Fig. S9 IR spectra for compounds ***L*-LnAg5-3D** and ***D*-LnAg5-3D**.

Table S1. The lifetimes of compounds **1-*L***, **2-*L*** and **3-*L*** at different excitation and emission wavelengths.

Compound	λ_{ex} / nm	λ_{em} / nm	Lifetime / μs
1-*L*	367	666	3.9
1-*L*	417	666	1.5
2-*L*	367	617	745.0
2-*L*	367	666	5.9
2-*L*	417	617	628.8
2-*L*	417	666	3.9
3-*L*	367	544	1196.9
3-*L*	367	666	5.8
3-*L*	417	544	223.0
3-*L*	417	666	1.8

Table S2. Crystallographic data for compounds **1-*L*** and **1-*D***.

Compound	**1-*L***	**1-*D***
Formula	$C_{30}H_{90}Ag_5Cl_2GdN_6O_{35}S_6$	$C_{30}H_{84}Ag_5Cl_2GdN_6O_{32}S_6$
FW	2054.93	2000.89
T/K	120	120
Cry. system	cubic	cubic
Space group	$P2_13$	$P2_13$
a /Å	20.2194(5)	20.354(5)
b /Å	20.2194(5)	20.354(5)
c /Å	20.2194(5)	20.354(5)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	8266.2(6)	8432(6)
Z	4	4
Dc/g cm^{-3}	1.651	1.576
μ/ mm^{-1}	17.069	16.689
Data/parameters	4951/191	4855/188
2θ/°	8.746-139.38	7.522-135.706
Obs. reflections	4951	4855
F(000)	4084.0	3964.0
GOF	1.029	0.937
R_1[I> 2σ(I)][a]	0.0706	0.0845
wR_2(All data)[b]	0.2102	0.2171

[a]$R_1=\Sigma||F_O| - |F_C||/\Sigma|F_O|$; [b]$wR_2=\{\Sigma[w(F_O^2 - F_C^2)^2]/\Sigma[w(F_O^2)^2]\}^{1/2}$

Table S3. Crystallographic data for compounds **2-*L*** and **2-*D***.

Compound	**2-*L***	**2-*D***
Formula	$C_{30}H_{90}Ag_5Cl_2EuN_6O_{35}S_6$	$C_{30}H_{108}Ag_5Cl_2EuN_6O_{44}S_6$
FW	2049.64	2211.79
T/K	120	120
Cry. system	cubic	cubic
Space group	$P2_13$	$P2_13$
a /Å	20.2017(6)	20.2305(7)
b /Å	20.2017(6)	20.2305(7)
c /Å	20.2017(6)	20.2305(7)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	8244.5(7)	8279.8(9)
Z	4	4
Dc/g cm^{-3}	1.651	1.774
μ/ mm^{-1}	17.356	17.415
Data/parameters	4494/191	4451/191
2θ/°	9.79-132.89	7.568-129.862
Obs. reflections	4494	4451
F(000)	4080.0	4440.0
GOF	1.039	1.021
R_1[I> 2σ(I)][a]	0.0786	0.0759
wR_2(All data)[b]	0.2241	0.2266

[a] $R_1=\Sigma||F_O| - |F_C||/\Sigma|F_O|$; [b] $wR_2=\{\Sigma[w(F_O^2 - F_C^2)^2]/\Sigma[w(F_O^2)^2]\}^{1/2}$

Table S4. Crystallographic data for compounds **3-*L*** and **3-*D***.

Compound	**3-*L***	**3-*D***
Formula	$C_{30}H_{82}Ag_5Cl_2TbN_6O_{31}S_6$	$C_{30}H_{84}Ag_5Cl_2TbN_6O_{32}S_6$
FW	1984.54	2002.56
T/K	150	150
Cry. system	cubic	cubic
Space group	$P2_13$	$P2_13$
a /Å	20.241(2)	20.285(3)
b /Å	20.241(2)	20.285(3)
c /Å	20.241(2)	20.285(3)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	8293(3)	8343(4)
Z	4	4
Dc/g cm^{-3}	1.590	1.594
μ/ mm^{-1}	15.976	15.888
Data/parameters	4916/192	4673/192
2θ/°	7.566-139.05	8.718-133.858
Obs. reflections	4916	4673
F(000)	3928.0	3968.0
GOF	1.041	1.122
R_1[I> 2σ(I)][a]	0.0886	0.1209
wR_2(All data)[b]	0.2497	0.3019

[a]$R_1=\Sigma||F_O| - |F_C||/\Sigma|F_O|$; [b]$wR_2=\{\Sigma[w(F_O^2 - F_C^2)^2]/\Sigma[w(F_O^2)^2]\}^{1/2}$

Table S5. Selected bond distances (Å) and band angles (°) of **1-*L***.

Ag1-S1[1]	2.480(11)	Gd1-O1[4]	2.463(17)
Ag1-S1	2.480(11)	Gd1-O3[3]	2.446(17)
Ag1-S1[2]	2.480(11)	Gd1-O3	2.446(17)
Ag2-S2[1]	2.456(11)	Gd1-O3[4]	2.446(17)
Ag2-S2	2.456(11)	Gd1-O4	2.471(19)
Ag2-S2[2]	2.456(11)	Gd1-O4[4]	2.471(19)
Ag3-S1	2.373(15)	Gd1-O4[3]	2.471(19)
Ag3-S2	2.385(15)	Gd2-O1[4]	1.75(2)
Gd1-O1	2.463(17)	Gd2-O1[3]	1.75(2)
Gd1-O1[3]	2.463(17)	Gd2-O1	1.75(2)

S1[2]-Ag1-S1	119.81(6)	O3-Gd1-O1[3]	143.9(7)
S1[1]-Ag1-S1	119.81(6)	O3[3]-Gd1-O1	74.7(6)
S1[2]-Ag1-S1	119.81(6)	O3[4]-Gd1-O1[4]	77.7(7)
S2-Ag2-S2[2]	119.03(12)	O3[4]-Gd1-O4[4]	50.7(6)
S2-Ag2-S2[1]	119.03(12)	O3[4]-Gd1-O3[3]	117.6(2)
S1-Ag3-S2	179.3(3)	O3[4]-Gd1-O4[3]	72.1(7)
O1[4]-Gd1-O1	75.5(8)	O3-Gd1-O4[3]	130.4(8)
O1[4]-Gd1-O4	124.8(7)	O4[4]-Gd1-O4	84.9(10)
O1[3]-Gd1-O4[3]	85.29(8)	O1[3]-Gd2-O1	119.57(14)
O1[3]-Gd1-O4	147.5(8)	O1[4]-Gd2-O1	119.57(14)
O1[4]-Gd1-O4[4]	85.2(8)		

Symmetry code:[1]-1/2+Y,-1/2-Z,-1-X; [2]-1-Z,1/2+X,-1/2-Y; [3]-1-Y,1/2+Z,-3/2-X; [4]-3/2-Z,-1-X,-1/2+Y

Table S6. Selected bond distances (Å) and band angles (°) of **1-*D***.

Gd1-O1	2.342(13)	Ag1-S2[4]	2.488(6)
Gd1-O1[1]	2.342(13)	Ag1-S2	2.489(6)
Gd1-O1[2]	2.342(12)	Ag1-S2[3]	2.488(6)
Gd1-O3[2]	2.490(15)	Ag2-S1[3]	2.479(6)
Gd1-O3[1]	2.490(15)	Ag2-S1	2.479(6)
Gd1-O3	2.490(15)	Ag2-S1[4]	2.479(6)
Gd1-O4	2.512(17)	Ag3-S1	2.366(7)
Gd1-O4[1]	2.512(17)	Ag3-S2	2.368(7)
Gd1-O4[2]	2.512(18)		

O1-Gd1-O1[1]	78.1(6)	O3-Gd1-O4[2]	126.8(6)
O1-Gd1-O3[2]	145.8(5)	O3[2]-Gd1-O4[2]	53.0(4)
O1-Gd1-O3[2]	73.3(5)	O3-Gd1-O4[1]	71.0(6)
O1[1]-Gd1-O4[2]	148.5(5)	O4[2]-Gd1-O4[1]	79.2(6)
O1-Gd1-O4	87.2(6)	S2[3]-Ag1-S2	119.04(6)
O1[2]-Gd1-O4[1]	126.2(5)	S1[3]-Ag2-S1[4]	119.77(3)
O3[2]-Gd1-O3[1]	117.4(2)	S1-Ag3-S2	179.6(3)
O3-Gd1-O3[2]	117.6(2)		

Symmetry code: [1]-1/2+Y,3/2-Z,1-X; [2]1-Z,1/2+X,3/2-Y; [3]-1/2+Z,1/2-X,1-Y; [4]1/2-Y,1-Z,1/2+X

Table S7. Selected bond distances (Å) and band angles (°) of **2-*L***.

Eu1-O4[3]	3.16(2)	Eu2-O1[4]	2.42(2)
Eu1-O4[4]	3.16(2)	Eu2-O1	2.42(2)
Eu1-O4	3.16(2)	Ag1-S1	2.530(12)
Eu1-O3	3.05(2)	Ag1-S1[1]	2.530(12)
Eu1-O3[4]	3.05(2)	Ag1-S1[2]	2.530(12)
Eu1-O3[3]	3.05(2)	Ag2-S21	2.423(10)
Eu2-O2[3]	2.51(2)	Ag2-S2[2]	2.423(10)
Eu2-O2[4]	2.51(2)	Ag2-S2	2.423(10)
Eu2-O2	2.51(2)	Ag3-S1	2.350(14)
Eu2-O1[3]	2.42(2)	Ag3-S2	2.431(15)

S1-Ag1-S1[1]	119.80(5)	O3[3]-Eu1-O3	82.7(7)
S2[1]-Ag2-S2[2]	118.96(12)	O2[4]-Eu2-O2[3]	79.0(8)
S1-Ag3-S2	178.2(4)	O1[4]-Eu2-O2[4]	88.9(7)
O4[3]-Eu1-O4	84.2(6)	O1-Eu2-O2[4]	151.0(7)
O3[3]-Eu1-O4[3]	167.5(5)	O1[4]-Eu2-O2	124.7(7)
O3-Eu1-O4	89.0(6)	O1-Eu2-O1[4]	76.4(8)
O3-Eu1-O4[3]	105.6(5)		

Symmetry code: [1]-1/2+Y,3/2-Z,1-X; [2]1-Z,1/2+X,3/2-Y; [3]+Z,+X,+Y; [4]+Y,+Z,+X

Table S8. Selected bond distances (Å) and band angles (°) of **2-*D***.

Eu1-O1[1]	2.55(2)	Ag3-S1	2.369(7)
Eu1-O1[2]	2.55(2)	Ag3-S2	2.362(8)
Eu1-O1	2.55(2)	Ag1-S1	2.446(6)
Eu1-O2[2]	2.502(18)	Ag1-S1[4]	2.446(6)
Eu1-O2[1]	2.502(18)	Ag1-S1[3]	2.446(6)
Eu1-O2	2.502(18)	Ag2-S2	2.485(7)
Eu1-O4	2.367(14)	Ag2-S2[4]	2.485(7)
Eu1-O4[1]	2.367(14)	Ag2-S2[3]	2.485(7)
Eu1-O4[2]	2.367(14)		

O1-Eu1-O1[1]	78.8(7)	O4[2]-Eu1-O2[1]	145.8(6)
O2-Eu1-O1[1]	126.1(6)	O4[1]-Eu1-O2[1]	78.5(6)
O2[2]-Eu1-O1[2]	51.7(4)	O4-Eu1-O2[1]	73.0(6)
O2[1]-Eu1-O1	72.5(6)	O4[1]-Eu1-O4	78.0(6)
O2[2]-Eu1-O2	117.4(2)	S1-Ag1-S1[3]	119.84 (3)
O4[2]-Eu1-O1	124.6(6)	S2-Ag2-S2[3]	118.98(7)
O4-Eu1-O1	87.9(6)	S2-Ag3-S1	179.3(2)
O4[2]-Eu1-O1[1]	150.4(6)		

Symmetry code: [1]+Z,+X,+Y; [2]+Y,+Z,+X; [3]1/2-Y,1-Z,1/2+X; [4]-1/2+Z,1/2-X,1-Y

Table S9. Selected bond distances (Å) and band angles (°) of **3-*L***.

Ag1-S1[1]	2.502(9)	Tb1-O2[4]	2.45(2)
Ag1-S1	2.502(9)	Tb1-O3[4]	2.35(2)
Ag1-S1[2]	2.502(9)	Tb1-O3[3]	2.35(2)
Ag2-S2	2.449(9)	Tb1-O3	2.35(2)
Ag2-S2[1]	2.449(9)	Tb2-O1[3]	2.38(3)
Ag2-S2[2]	2.449(9)	Tb2-O1[4]	2.38(3)
Ag3-S1	2.407(14)	Tb2-O1	2.38(3)
Ag3-S2	2.356(13)	Tb2-O4[4]	2.77(3)
Tb1-O2[3]	2.45(2)	Tb2-O4	2.77(3)
Tb1-O2	2.45(2)	Tb2-O4[3]	2.77(3)

S1[1]-Ag1-S1[2]	118.79(12)	O3[4]-Tb1-O3[3]	118.2(3)
S2[2]-Ag2-S2[1]	119.92(3)	O1-Tb2-O4[3]	69.3(7)
S2-Ag3-S1	179.7(3)	O1[3]-Tb2-O4	139.9(10)
O2[3]-Tb1-O2[4]	81.4(8)	O1-Tb2-O1[3]	98.8(11)
O3-Tb1-O2[4]	129.2(7)	O1[4]-Tb2-O4[4]	49.0(5)
O3[4]-Tb1-O2[4]	51.9(4)	O4[4]-Tb2-O4	117.2(3)
O3[3]-Tb1-O2	73.7(8)		

Symmetry code: [1]+Z,+X,+Y; [2]+Y,+Z,+X; [3]1-Y,-1/2+Z,3/2-X; [4]3/2-Z,1-X,1/2+Y

Table S10. Selected bond distances (Å) and band angles (°) of **3-*D***.

Tb1-O1	2.40(3)	Tb2-O4^{2}	1.79(4)
Tb1-O1^{1}	2.40(3)	Tb2-O4	1.79(4)
Tb1-O1^{2}	2.40(3)	Ag1-S1^{3}	2.487(9)
Tb1-O2	2.44(3)	Ag1-S1	2.487(9)
Tb1-O2^{1}	2.44(3)	Ag1-S1^{4}	2.487(9)
Tb1-O2^{2}	2.44(3)	Ag2-S2^{4}	2.476(10)
Tb1-O4^{1}	2.39(4)	Ag2-S2^{3}	2.476(10)
Tb1-O4^{2}	2.39(4)	Ag2-S2	2.476(10)
Tb1-O4	2.39(4)	Ag3-S1	2.408(12)
Tb2-O4^{1}	1.79(4)	Ag3-S2	2.381(12)

O1-Tb1-O1^{1}	82.9(11)	O4^{1}-Tb1-O2	63.0(11)
O1^{2}-Tb1-O2^{1}	73.5(9)	O4-Tb1-O2^{1}	142.9(11)
O1-Tb1-O2^{1}	130.2(10)	O4^{2}-Tb1-O2^{2}	85.5(11)
O1^{1}-Tb1-O2^{1}	51.6(8)	O4^{1}-Tb1-O4	80.8(14)
O2^{1}-Tb1-O2^{2}	118.2(3)	O4^{2}-Tb2-O4^{1}	119.8(2)
O4^{2}-Tb1-O1	158.8(10)	S1^{3}-Ag1-S1	118.57(12)
O4-Tb1-O1	86.7(11)	S2^{3}-Ag2-S2^{4}	119.78(5)
O4-Tb1-O1^{2}	114.1(11)	S2-Ag3-S1	178.9(4)

Symmetry code: ^{1}+Z,+X,+Y; ^{2}+Y,+Z,+X; ^{3}1/2-Y,1-Z,1/2+X; ^{4}-1/2+Z,1/2-X,1-Y