Supporting Information Available: bond distances and angles (Table S2), percentage compositions of orbitals (MO) in the HOMO-LUMO region (Table S5) of optimized geometry of $Ln(OTf)_3$ where Ln = La, Ce, Nd, Eu, Gd, Er, Yb and Lu.

	La	Ce	Nd	Eu	Gd	Er	Yb	Lu
	(OTf) ₃	(OTf) ₃	(OTf) ₃ *	(OTf) ₃ *	(OTf) ₃	(OTf) ₃	(OTf) ₃	(OTf)
				× ,-				3
Ln-O2	2.491	2.464	2.442	2.437	2.375	2.344	2.349	2.290
				$(2.48)^{**}$				(2.34)
								**
Ln-O3	2.490	2.463	2.437	2.431	2.377	2.341	2.346	2.292
Ln-O20	2.491	2.464	2.447	2.444	2.377	2.344	2.346	2.291
Ln-O19	2.490	2.464	2.442	2.429	2.374	2.344	2.348	2.290
Ln-O12	2.490	2.466	2.443	2.432	2.377	2.342	2.346	2.292
Ln-O11	2.491	2.464	2.441	2.440	2.375	2.344	2.349	2.291
S1-O2	1.514	1.514	1.515	1.511	1.516	1.515	1.513	1.518
S1-O3	1.514	1.515	1.515	1.512	1.515	1.515	1.514	1.518
S17-O20	1.514	1.515	1.514	1.510	1.515	1.515	1.513	1.518
S17-O19	1.514	1.515	1.515	1.513	1.516	1.515	1.513	1.517
S9-O12	1.514	1.514	1.514	1.512	1.515	1.515	1.513	1.518
S9-O11	1.514	1.514	1.515	1.511	1.516	1.515	1.513	1.517
S1-O4	1.440	1.440	1.440	1.442	1.440	1.441	1.442	1.439
S17-O18	1.441	1.440	1.440	1.442	1.440	1.441	1.442	1.439
S9-O10	1.440	1.440	1.440	1.442	1.440	1.441	1.442	1.439
S-Ln	3.092	3.065	3.040	3.030	2.972	2.936	2.938	2.883
S1(17,9)-C5(21,13)	1.887	1.888	1.888	1.888	1.888	1.889	1.889	1.889
$O_2 I_m O_2$	57.0	506	50.2	50.2	60.9	61.6	61.5	62.1
03-LII-02	57.9	38.0	39.5	39.5	00.8	01.0	01.5	05.1
011-Ln-O12	57.9	58.5	59.1	59.2	60.8	61.6	61.5	63.1
O19-Ln-O20	57.9	58.6	59.1	59.2	60.8	61.6	61.5	63.1
O3-S1-O2	105.7	105.5	105.6	105.6	104.9	104.8	104.9	104.3
011-S9-O12	105.7	105.5	105.5	105.5	104.9	104.8	104.9	104.3
019-\$17-020	105.7	105.5	105.5	105.6	104.9	104.8	10/ 9	104.3
019-517-020	105.7	105.5	105.5	105.0	104.9	104.0	104.9	104.5
Ln-O3-S1-O2	0.6	0.8	0.3	0.8	0.2	-0.6	-1.3	-0.5
In-011-89-012	-0.6	-1.0	-0.0	0.0	-0.2	0.8	_1 3	0.5
Lii-011-37-012	-0.0	-1.0	-0.0	0.0	-0.2	0.0	-1.5	0.5
Ln-O19-S17-O20	-0.7	-0.3	0.6	1.1	-0.2	0.8	1.2	0.5

*: geometry in conformer **: EXAFS data¹⁸

Table S2: Main Geometry Parameters of Ln(OTf)₃.

										Fie	CITO	nic	Supple	eme	nta	ry in	torr	pati	on ti iotv		alto	n Iran	sac	hon	s					1
17β	77β	0	-4.726	100	0		77β		-3.896	100	0	s joi	umari: 818 8	, U	-7.486	94 70	yai 9	0		0	Jner	nistry .	2011	,93 ^c	7				5	Lf) ₃
	76β		-4.728	100	0		76β	0	-4071	100	0		80ß		-7.537	98	2	0	0	0		LUMO+1	0	-1.7	7	0	8	0	1:	f Ln(O]
β	75β		-8.517	0	100		75β		-8.663	0	100		79β (OMOS)		-7.698	100	0	0	0	0				9						gion of
f) ₃	74β	1	-8.858	2	86	f) ₃	74β	1	-8.858	0	100	f_{3}	78β	-	-7.719	100	0	0	0	0	f) ₃	LUMO	0	-2.84	82	1	12	5	0	UMO re
Ce(OT	78 α		-5.024	100	0	Eu(OT	83a		-3.097	95	0	Er(OT	84α		-1.727	65	6	18	0	8	Lu(OT			48	0	0	0	0	0	OMO-LI
	77 α	0	-5.100	100	0		82α	0	-7.800	70	30		83α	0	-2.633	83	1	13	0	3		ОМОН	2	-8.6	10					the H
α	76 α SOMO)		-5.213	0	100		81α (OMO)		-7.975	91	6	-	82α		-8.558	11	89	0	0	0										MO) in
	$\frac{5 \alpha}{1}$.522	100	00 0		0α (S	-		94	9		1α	1	873	9	94	0	0	0		40-1 2	2	-8.943	1	66	0	0	0	rbitals (
	7:		×,			<u>.</u>	∞		-7.			_	∞		8		Š,		_			NOH								ed o
LUMO+1	10+1		831	00	0		77β	0	-5.034	100	0		77β	0	-5.866	100	0	0	0	0		83β	0	-2.545	82	1	14	ε	0	f select
	-	- . 3.	1	-		76β		-5.228	100	0		76β		-5.866	100	0	0	0	0		82β		-8.015	68	32	0	0	0	tions of	
	Ю		32	0			75β		-8.596	0	100		75β		-8.619	2	98	0	0	0		81β (SOMO)		-8.149	91	6	0	0	0	composi
$(f)_3$	ΓΩ	0	-3.8	10	0	$[f]_3$	74β	1	-8.852	1.5	98.5	$(f)_3$	74β	-	-8.943	2	98	0	0	0	[f] ₃	80ß	1	-8.150	88	12	0	0	0	centage
La(O]	ОМ		183		00	O)pN	80α		-6.542	100	0	Gd(O	84α		-2.242	60	4	3.5	2.5	0	Yb(O	84α		1.652	59	8	21	11	0	and pere
	OH		-8.)	1(79α		-6.662	100	0		83α		-3.430	95	0	5	0	0		83 α	0	2.605 -	83	1.2	13	2.8	0	, eV) a
-1		33		5		78α SOMO)		-6.725	100	0		82α (SOMO)		-8.535	2	98	0	0	0		82α		8.430 -	82	18	0	0	0	ergies (e	
	HOM	2	-8.8	1.5	98.			-	9				7	1	4								1	0						Ene
							77α		-6.75	100	0		81c		-8.87	2	98	0	0	0		81α		-8.43	82	18	0	0	0	e S5:
	OMs	Occup	En eV	Ln %	0		OMs	Occup	En eV	Ln %	0		OMs	Occup	En eV	Ln %	0	S	Ц	С		OMs	Occup	En eV	Ln %	0	S	С	F	Table

Electronic Supplementary Information for Dalton Transactions

La(ClO4 16)3 -constrain		
Cl	-2.56586625	2.20204883	1.45910782
0	-3.14616837	1.81425359	2.72454716
0	-1.99222915	3.60213688	1.37118194
0	-1.39612164	1.35033508	0.98111161
0	-3.51015277	2.17151296	0.26343800
Cl	-0.38784156	5.38947451	-1.28798413
0	0.18223346	6.70783943	-1.44766734
0	0.24538219	4.52354615	-0.20568489
0	-1.86677102	5.35020547	-0.92262291
0	-0.33734389	4.47282374	-2.49391158
La	-1.47590012	2.90237047	-0.95027715
C1	-1.46727335	1.11285696	-3.01936579
0	-1.45368183	0.18095744	-4.12387875
0	-2.09738633	0.63191385	-1.72759473
0	-0.10126489	1.59386188	-2.54515151
0	-2.21216643	2.41891475	-3.26752195
La(Cl04)3 -no-constrain		
16 C1) (5766775	0 07016076	1 00004000
0	-2.05/00//5	2.37213075	2 2896/38/
0	-2 61763250	2 36933758	2.20004004
0	-1 21605122	2 10662187	1 38924898
0	-3.35295671	2.96814209	0.66021190
Cl	-0.15884253	5.68691741	-1.62298054
0	-0.09150640	6.77569833	-0.65833238
0	0.50153532	4.40616021	-1.02498912
0	-1.63797016	5.22232215	-1.79714049
0	0.42385011	5.98373622	-2.92410447
La	-1.46596904	2.89984142	-0.94639024
Cl	-1.58280937	0.64098450	-3.14145377
0	-1.06568738	0.83106123	-4.48943346
0	-2.15797398	-0.67202033	-2.88500669
0	-0.46503111	0.94458554	-2.09624138
0	-2.62748046	1.75183250	-2.81183799
) constrain		
)-CONSTIAIN		
20	-2 40108079	2 25059557	1 2/809783
с С	-3 13678636	1 69426100	2 90866687
ਤ ਸ	-2 17839474	1 74819096	3 84117960
т F	-3 59133797	0 44221869	2 78690919
F	-4.13956440	2.51966379	3.23132654
0	-1.85971497	3.62709218	1.24312359
0	-1.26361788	1.38370163	0.82892607
0	-3.41556953	2.22820404	0.15630443
S	-0.47736865	5.14330163	-1.25119056
С	0.26557619	6.88306522	-1.42231407
F	0.14659089	7.52470625	-0.25472842
F	-0.39906153	7.54076147	-2.37974112
F	1.55664257	6.76689085	-1.75505460
0	0.22834481	4.34065551	-0.21268729
0	-1.92131147	5.19122626	-0.88495038

0	-0 41856701	4 32179180	-2 47998734
U T 11	1 46207800	2 20750160	0 04429242
ц	1 40070000	1 20070200	-0.94430242
5	-1.49878006	1.29670386	-2.82633133
C	-1.49558522	0.11204329	-4.31069639
F	-0.80394448	-0.98527569	-3.98156279
F	-0.92281343	0.72222896	-5.35419153
F	-2.76072406	-0.21196874	-4.60354148
0	-2.10539262	0.74401856	-1.59573235
0	-0.11707883	1.69451768	-2.43414976
0	-2.26629564	2.54161804	-3.11283367
Τηι (ΟΤΕ3)-no-constain-com	lformer1	
25	,		
2 J	-2 233/3806	3 20864802	1 9191/359
2	-2.23343800	1 67672675	2.50066175
0	-3.03414207	1.6/6/36/5	2.58066175
F.	-2.29107322	1.26005608	3.61564697
F	-3.10983000	0.69540697	1.65756878
F	-4.26745960	1.98816721	3.00381707
0	-2.18919587	4.21010679	2.85098765
0	-0.91611690	2.69986523	1.26231607
0	-3.07400910	3.49130010	0.58674745
S	-0 18048154	5 09312027	-2 33161462
C	0 12090996	6 62411279	-1 26625638
E E	-0.24041569	6 40655224	-0.01601167
r T	-0.34041308	0.40055554	-0.01091107
F.	-0.52319158	7.66926495	-1.80453953
F.	1.43643375	6.87732390	-1.21865540
0	0.47198785	3.96599854	-1.55278853
0	-1.66875749	4.83252894	-2.18957852
0	0.33109465	5.39302198	-3.64302402
Lu	-1.47480458	2.91389062	-0.95105958
S	-2.02126992	0.44475774	-2.34210586
С	-1.43486451	0.40701810	-4.13764495
г Г	-0 54734090	-0 58588106	-4 29055029
- F	-0 85231761	1 58307118	-1 15107581
- -	-2 49902221	0.20192262	-1 0/1220//
F O	-2.40003221	0.20193203	-4.94133944
0	-2.63168/1/	-0.83203395	-2.07904963
0	-0.77787306	0.81522317	-1.55454974
0	-2.89545622	1.68243117	-2.26388158
Lu (OTF3)-no-constrain-co	onformer2	
25			
С	1.14259146	1.42121948	-0.13935188
S	2.20259562	-0.04851830	0.39846099
0	3 31082341	0 58483278	1 21941092
U.11	/ 98937338	0 19880420	-0 29/3/090
	E 00021724	1 00000420	
0	5.09031734	1.02250711	-1.91915000
S	5.97092059	2.77620755	-1.13516904
0	5.57460977	4.15777435	-1.05/22712
С	7.62118607	2.73710495	-2.05541458
F	8.53899951	3.40930482	-1.34592849
F	7.46567365	3.31161813	-3.25621792
F	8.02524986	1.46170737	-2.21856336
0	6.05240668	-1.34475404	1.03767903
S	6.68855128	-2.12668041	-0.09570009
0	6 56720092	-3 56066347	-0 08384597
0	6 25797001	_1 3871/0/0	_1 3500504001
0	0.40/9/004	1.00/14940	T. JJUJJ47T

F	0.56585634	1.96508049	0.94176827
F	0.19865380	0.99737849	-0.99138034
F	1.91565932	2.34264910	-0.74727369
0	1.32100362	-0.98063189	1.05051849
0	2.89074618	-0.49588755	-0.87997986
0	6.25403986	2.04544828	0.16652307
С	8.53210160	-1.73820157	0.05673975
F	9.17693376	-2.22897607	-1.01157869
F	8.71610434	-0.40388659	0.11767378
F	9.00932957	-2.30411984	1.17372765