Supplementary Information for《The Interplay of Steric hindrance and Electronic Effects in Asymmetric diglycolamides, Revealed through Their Ln(III) Coordination and Extraction Behavior》

Chuang Zhao[a,b], Jiale Song[a,b], Yaoyang Liu[a,b], Yu Zhou[a,b], Tingting Liu[a,b], Meng Zhang[a,b], Caishan Jiao[a,b], Yang Gao[a,b,*], Qunyan Wu[d], Weifang Zheng[a,c,*]

[a] College of Nuclear Science and Technology, Harbin Engineering University, Harbin 150001, P.R. China;

[b] Heilongjiang Provincial Key Laboratory of Nuclear Chemical Engineering and Radiochemistry, Harbin 150001, P.R. China;

[c] Department of Radiochemistry, China Institute of Atomic Energy, Beijing, 102413, P.R. China

[d] Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, P.R. China

1 Ligand synthesis related

1.1 Synthesis scheme

Two corresponding secondary amines need to be synthesized: 1) The corresponding bromoalkanes (3-bromooctane, bromoisooctane) are reacted with methylamine alcohol in a molar ratio of 1:8 in a reaction vessel at 110°C for 30 hours. 2) The solution is then removed, and unreacted methylamine alcohol is evaporated using a rotary evaporator. The product is dissolved in chloroform and washed with saturated Na_2CO_3 solution. 3) Finally, the fraction collected at 195°C by distillation is the desired secondary amine ((1-ethylhexyl)(methyl)amine and (2-ethylhexyl)(methyl)amine).

1.2 ^{1}H-NMR

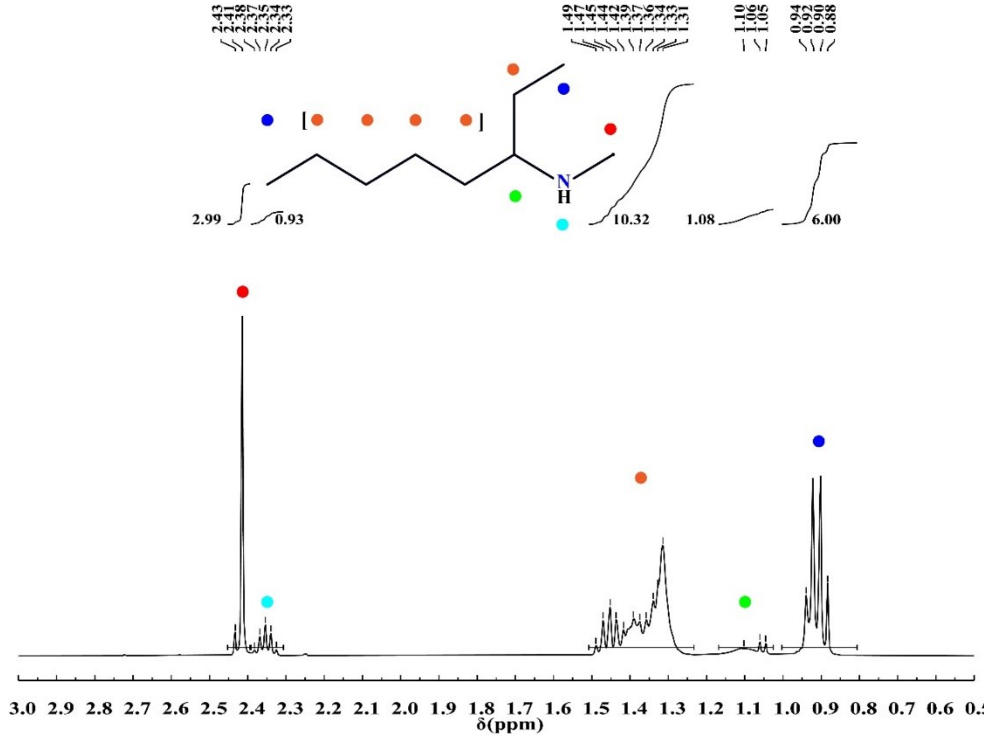

Fig. S1. The ^{1}H-NMR spectrum of 1-Ethylhexylmethylamine (solvent: $CDCl_3$, 500MHz)

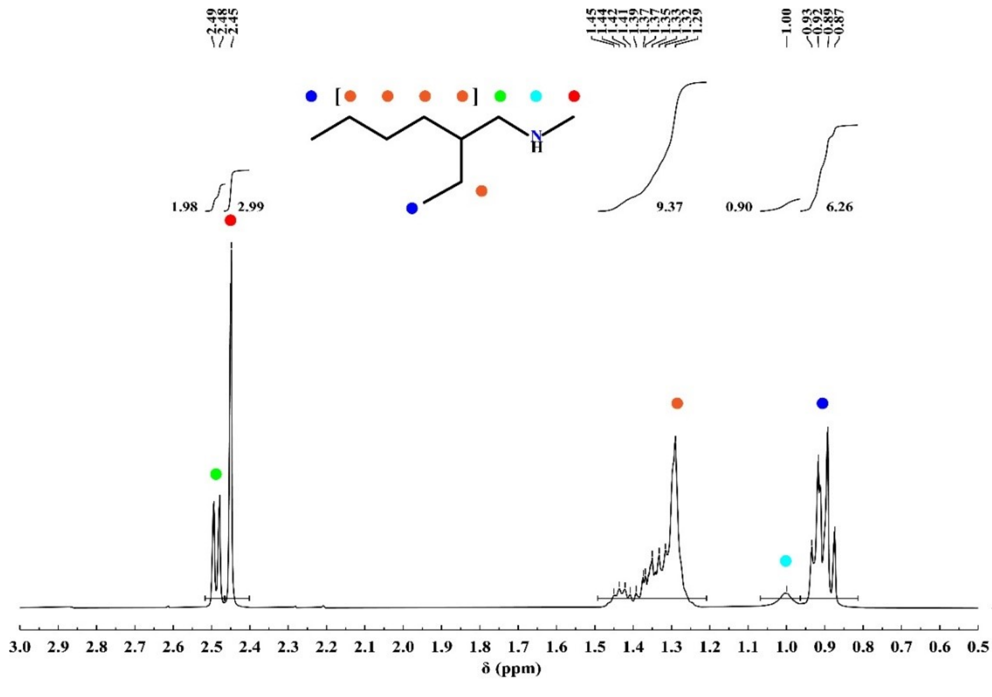

Fig. S2. The 1H-NMR spectrum of 1-Ethylhexylmethylamine (solvent: CDCl3, 500MHz)

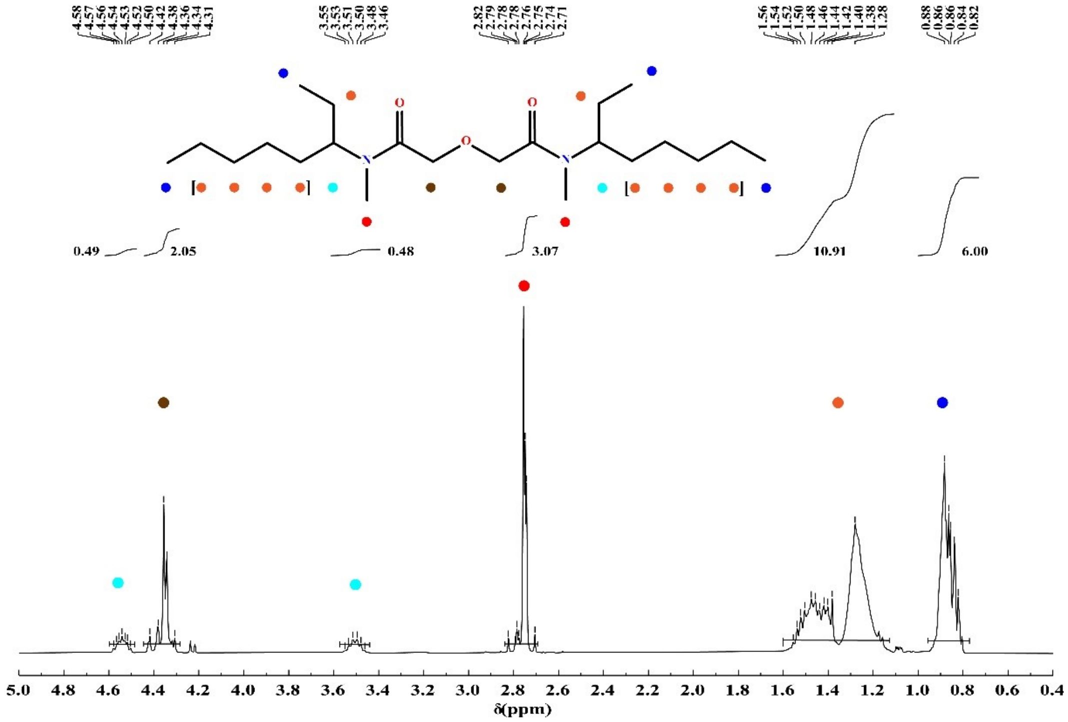

Fig. S3. The ^{1}H-NMR spectrum of L_1 (solvent: $CDCl_3$, 500MHz)

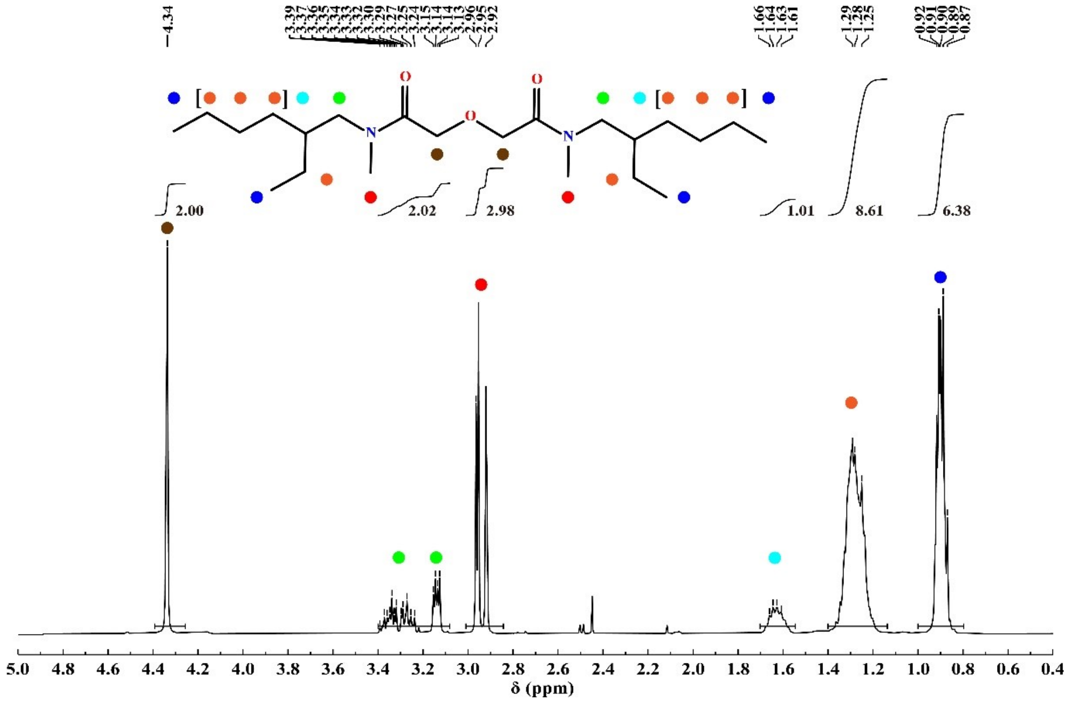

Fig S4. The ^{1}H-NMR spectrum of L_2 (solvent: $CDCl_3$, 500MHz)

2 DFT Calculation Supplementary Data

2.1 Geometrically optimized complexes structure

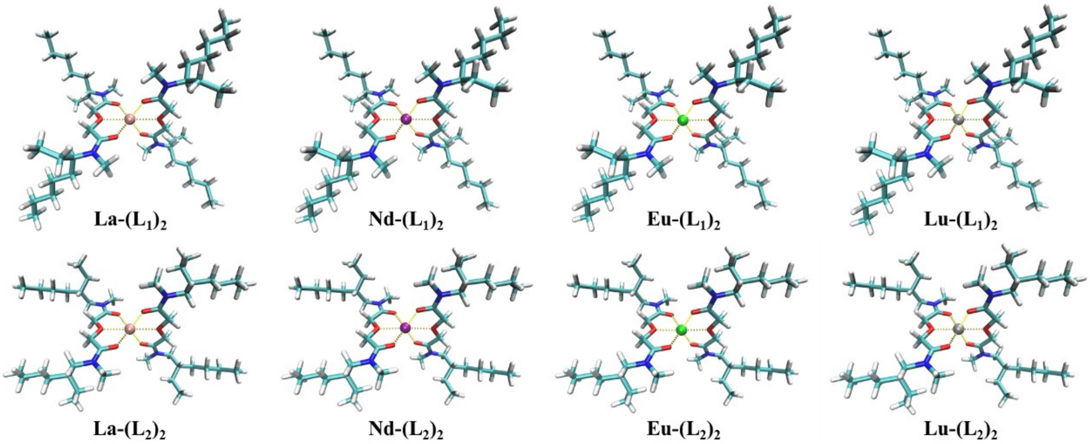

Fig. S5. The optimized structures of $[Ln\text{-}(L_n)_2]^{3+}$ (n=1 or 2)at the B3LYP/6-311G(d)/RECP level of theory (cyan: C, white: H, blue: N, red: O, pink: La, purple: Nd, green: Eu, silver: Lu).SI

2.2 IGMH diagram of complexes

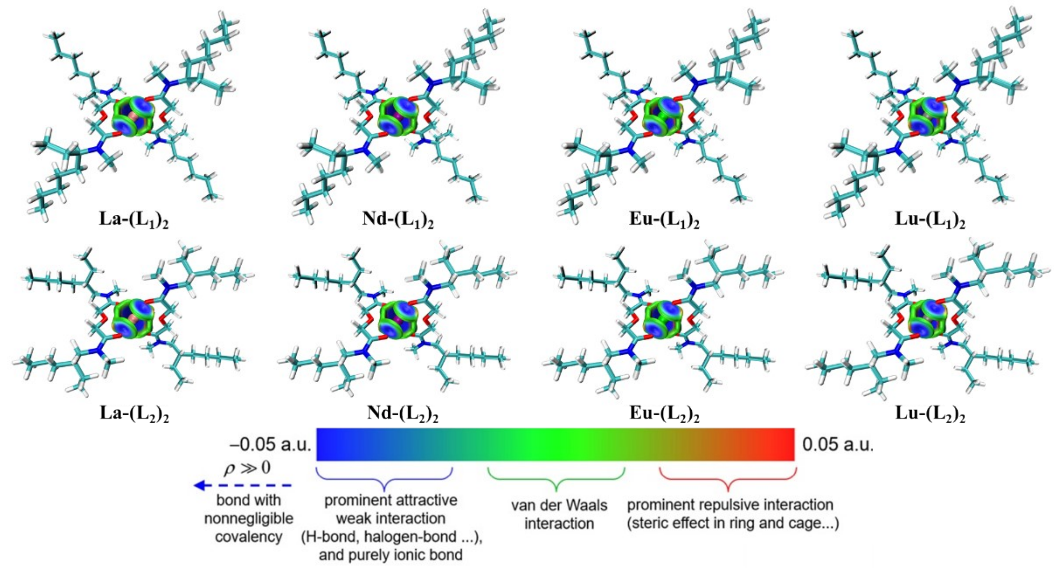

Fig. S6. IGMH Analysis of Ligands and Ln(III) Complexes (siovalue=0.002 a.u.)

2.3 The table required for bond analysis of complexes

Table S1. Bond lengths of the complexes (Å)

Ligands	Ln(III)	$Ln\text{-}O_{ether}$	$Ln\text{-}O_{amide1}$	$Ln\text{-}O_{amide2}$	$Ln\text{-}O_{average}$
L_1	La	2.6108	2.3584	2.3583	2.5266
	Nd	2.5317	2.2970	2.2970	2.4535
	Eu	2.4708	2.2644	2.2644	2.4020
	Lu	2.3544	2.1657	2.1657	2.2915
L_2	La	2.6062	2.3618	2.3618	2.5247
	Nd	2.5277	2.3004	2.3004	2.4519
	Eu	2.4609	2.2671	2.2671	2.3963
	Lu	2.3514	2.1681	2.1681	2.2903

Table S2. Calculated MBOs of the O_{ether}–Ln and O_{amide}–Ln bonds in the complexes (a.u.)

Ln^{3+}	Bond	L_1		L_2	
		MBO	Average	MBO	Average
	La-O_{ether}	0.1901		0.1932	
La	La-$O_{amide, 1}$	0.4945	0.3423	0.4894	0.3413
	La-$O_{amide, 2}$	0.4945		0.4894	
	Nd-O_{ether}	0.2033		0.2052	
Nd	Nd-$O_{amide, 1}$	0.4995	0.3505	0.4930	0.3492
	Nd-$O_{amide, 2}$	0.4960		0.4940	
	Eu-O_{ether}	0.2106		0.2137	
Eu	Eu-$O_{amide, 1}$	0.4855	0.3487	0.4775	0.3456
	Eu-$O_{amide, 2}$	0.4883		0.4743	
	Lu-O_{ether}	0.2370		0.2379	
Lu	Lu-$O_{amide, 1}$	0.5170	0.3770	0.5115	0.3747
	Lu-$O_{amide, 2}$	0.5170		0.5115	

It is generally believed that when $\rho(r)>0.20$ a.u. and $\nabla^2\rho(r)<0$ at the critical point of the bond, it indicates open-shell (covalent) interactions, while $\rho(r)<0.10$ a.u. and $\nabla^2\rho(r)>0$ correspond to closed-shell interactions, which are considered to be electrostatic, hydrogen bonding, and van der Waals interactions. Additionally, the values of $|V|/G$ and H can also reflect the nature of bonding. Studies have found that when $|V|/G<1$, bonding corresponds to closed-shell interactions; when $1<|V|/G<2$, it represents electrostatic interactions with covalent characteristics; and when $|V|/G>2$, it is considered as covalent interaction. When the total energy density $H>0$, it is generally regarded as non-covalent interaction, and conversely, as covalent interaction[1–3].

Table S3. The QTAIM analysis results of M-O_{ether}, M-O_{amide1} and M-O_{amide2} in the optimized complexes (a.u.)

Ligand	Bond	avergeρ(r)	$\nabla^2\rho$(r)	H	V	G	$\|V\|/G$
	La-O_{ether}	0.03494	0.14398	0.00227	-0.03145	0.03372	0.93254
	La-$O_{amide,1}$	0.06352	0.23246	-0.00478	-0.06767	0.06289	1.07593
	La-$O_{amide,2}$	0.06352	0.23246	-0.00478	-0.06767	0.06289	1.07593
	Nd-O_{ether}	0.03851	0.17096	0.00230	-0.03814	0.04044	0.94310
	Nd-$O_{amide,1}$	0.06789	0.26976	-0.00586	-0.07915	0.07330	1.07989
	Nd-$O_{amide,2}$	0.06791	0.26884	-0.00588	-0.07896	0.07309	1.08042
L_1	Eu-O_{ether}	0.04077	0.18717	0.00231	-0.04216	0.04448	0.94796
	Eu-$O_{amide,1}$	0.06984	0.29396	-0.00627	-0.08603	0.07976	1.07862
	Eu-$O_{amide,2}$	0.06984	0.29397	-0.00627	-0.08603	0.07976	1.07862
	Lu-O_{ether}	0.04577	0.22939	0.00227	-0.05281	0.05508	0.95884
	Lu-$O_{amide,1}$	0.07610	0.35637	-0.00802	-0.10513	0.09711	1.08257
	Lu-$O_{amide,2}$	0.07610	0.35637	-0.00802	-0.10513	0.09711	1.08257
	La-O_{ether}	0.03535	0.14527	0.00222	-0.03187	0.03410	0.93480
	La-$O_{amide,1}$	0.06305	0.23076	-0.00461	-0.06690	0.06230	1.07395
L_2	La-$O_{amide,2}$	0.06305	0.23076	-0.00461	-0.06690	0.06230	1.07395
	Nd-O_{ether}	0.03851	0.17096	0.00230	-0.03814	0.04044	0.94310
	Nd-$O_{amide,1}$	0.06789	0.26976	-0.00586	-0.07915	0.07330	1.07989

Nd-$O_{amide,2}$	0.06791	0.26884	-0.00588	-0.07896	0.07309	1.08042
Eu-O_{ether}	0.04180	0.19151	0.00217	-0.04354	0.04571	0.95254
Eu-$O_{amide,1}$	0.06940	0.29217	-0.00611	-0.08527	0.07916	1.07723
Eu-$O_{amide,2}$	0.06940	0.29217	-0.00611	-0.08527	0.07915	1.07723
Lu-O_{ether}	0.04618	0.23099	0.00216	-0.05342	0.05558	0.96106
Lu-$O_{amide,1}$	0.07566	0.35406	-0.00785	-0.10421	0.09636	1.08145
Lu-$O_{amide,2}$	0.07566	0.35406	-0.00785	-0.10421	0.09636	1.08144

Reference:

1 W. Koch, G. Frenking, J. Gauss, D. Cremer and J. R. Collins, *J. Am. Chem. Soc.*, 1987, **109**, 5917–5934.

2 P.-W. Huang, C.-Z. Wang, Q.-Y. Wu, J.-H. Lan, G. Song, Z.-F. Chai and W.-Q. Shi, *Phys. Chem. Chem. Phys.*, 2018, **20**, 14031–14039.

3 Y. Liu, S. Liu, Z. Liu, C. Zhao, C. Li, Y. Zhou, C. Jiao, Y. Gao, H. He and S. Zhang, *RSC Adv.*, 2021, **11**, 27969–27977.