Supporting information for

Impact of nuclear number on SHG and THG performances: A comparative study of chiral mono- and dinuclear Tb^{III} complexes with identical organic ligands

Taoyu Wang,[a,b] Yanhong Peng,*[a,b] Yang Wang,[c] Congli Gao[c] and Xi-Li Li*[c]

[a]Guangdong Provincial Laboratory of Chemistry and Fine Chemical Engineering Jieyang Center, Jieyang 515200, China

[b]School of Advanced Manufacturing, Guangdong University of Technology, Jieyang 515200, China. E-mail: taoyuw@gdut.edu.cn

[c]Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450002, PR China. E-mail: lixl@zzuli.edu.cn

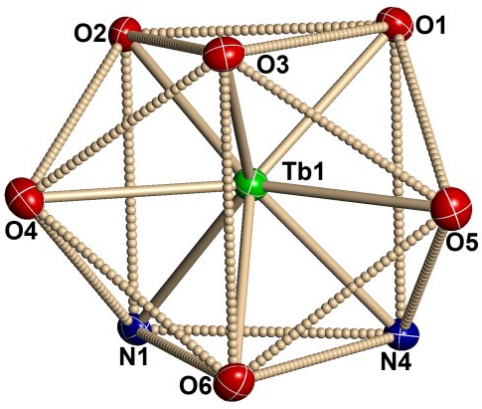

Fig. S1 Coordination geometry of Tb1 in **S-Tb-1**.

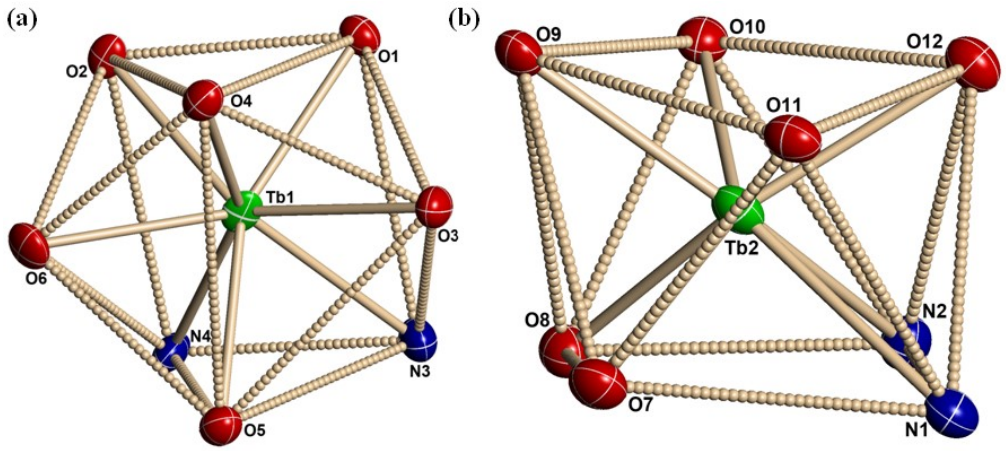

Fig. S2 Coordination geometries of Tb1 (a) and Tb2 (b) in **S-Tb-2**.

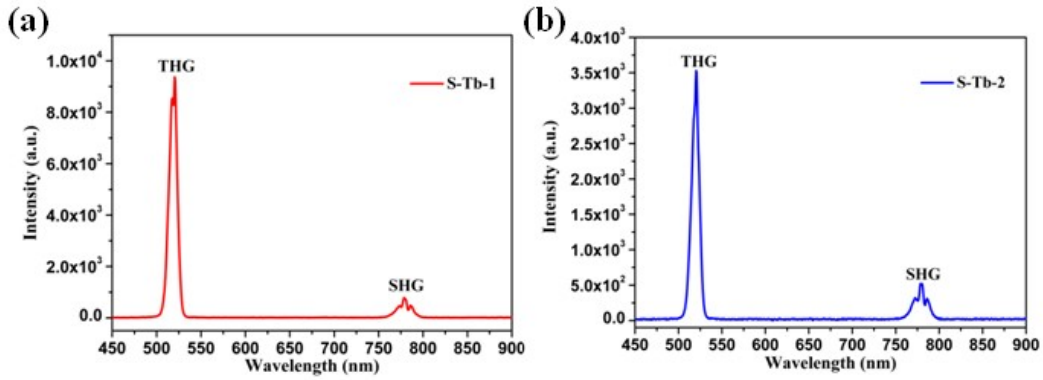

Fig. S3 Under excitation at λ = 1550 nm (T_{int} = 0.5 s), THG and SHG spectra of **S-Tb-1** (a) and **S-Tb-2** (b).

Table S1 Crystallographic data and structure refinement parameters for **S-Tb-1** and **S-Tb-2**.

Complexes	**S-Tb-1**	**S-Tb-2**
Chemical formula	$C_{73}H_{67}N_4O_8Tb$	$C_{108}H_{114}N_4O_{16}Tb_2$
Formula weight	1287.22	2151.89
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1$
a (Å)	17.0372(3)	13.8331(12)
b (Å)	17.9771(4)	20.3348(13)
c (Å)	21.5515(4)	20.2449(12)
α (deg)	90	90
β (deg)	90	97.612(13)
γ (deg)	90	90
V (Å^3)	6600.8(2)	5644.6(7)
Z	4	2
D_c (g cm^{-3})	1.295	1.266
μ (mm^{-1})	1.128	1.305
F(000)	2648	2196
Reflections collected	20541	24331
Independent reflections	12985	20125
Data/restraints/parameters	12985/30/806	20125/31/1319
GOF	1.001	1.097
R_1[I > = 2σ(I)][a]	0.0411	0.0466
wR_2[I > = 2σ(I)][b]	0.0897	0.1033
Flack parameter	0.018(8)	0.008(7)
CCDC	2465233	2465234

[a]$R_1 = \sum||Fo|-|Fc||/\sum|Fo|$. [b]w$R_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (°) for **S-Tb-1** and **S-Tb-2**.

Bond lengths for **S-Tb-1**					
Tb(1)─O(1)	2.303(5)	Tb(1)─O(2)	2.347(6)	Tb(1)─O(3)	2.309(5)
Tb(1)─O(4)	2.369(5)	Tb(1)─O(5)	2.361(5)	Tb(1)─O(6)	2.336(5)
Tb(1)─N(1)	2.570(7)	Tb(1)─N(4)	2.600(6)		
Bond lengths for **S-Tb-2**					
Tb(1)─O(1)	2.323(5)	Tb(1)─O(2)	2.344(5)	Tb(1)─O(3)	2.364(5)
Tb(1)─O(4)	2.294(6)	Tb(1)─O(5)	2.354(5)	Tb(1)─O(6)	2.323(5)
Tb(1)─N(3)	2.693(8)	Tb(1)─N(4)	2.633(7)	Tb(2)─O(7)	2.284(6)
Tb(2)─O(8)	2.332(6)	Tb(2)─O(9)	2.295(6)	Tb(2)─O(10)	2.315(5)
Tb(2)─O(11)	2.353(6)	Tb(2)─O(12)	2.305(5)	Tb(2)─N(1)	2.549(7)
Tb(2)─N(2)	2.590(7)				
Bond angles for **S-Tb-1**					
O(1)-Tb(1)-O(2)	71.79(17)	O(3)-Tb(1)-O(4)	71.03(18)	O(5)-Tb(1)-O(6)	72.27(19)
O(1)-Tb(1)-O(5)	74.81(18)	O(2)-Tb(1)-O(4)	72.53(17)	N(1)-Tb(1)-N(4)	62.28(19)
N(4)-Tb(1)-O(5)	75.8(2)	N(1)-Tb(1)-O(4)	75.33(18)	O(1)-Tb(1)-N(4)	79.88(19)
Bond angles for **S-Tb-2**					
O(1)-Tb(1)-O(2)	69.28(19)	O(3)-Tb(1)-O(4)	72.4(2)	O(5)-Tb(1)-O(6)	72.0(2)
O(2)-Tb(1)-O(4)	83.75(19)	O(1)-Tb(1)-O(3)	72.5(2)	N(3)-Tb(1)-N(4)	59.8(2)
N(4)-Tb(1)-O(2)	83.9(2)	N(3)-Tb(1)-O(1)	82.0(2)	N(3)-Tb(1)-O(3)	73.3(2)
O(7)-Tb(2)-O(8)	73.1(2)	O(9)-Tb(2)-O(10)	73.72(19)	O(11)-Tb(2)-O(12)	73.38(19)
O(9)-Tb(2)-O(11)	79.2(2)	O(10)-Tb(2)-O(12)	77.03(19)	N(1)-Tb(2)-O(7)	77.7(2)
N(2)-Tb(2)-O(8)	71.7(2)	N(2)-Tb(2)-O(12)	75.8(2)	N(1)-Tb(2)-O(11)	77.6(2)

Table S3 Continuous shape measures calculation for Tb1 in **S-Tb-1**. The lowest CShMs value is marked in red.

OP-8	1 D_{8h}	Octagon
HPY-8	2 C_{7v}	Heptagonal pyramid
HBPY-8	3 D_{6h}	Hexagonal bipyramid
CU-8	4 O_h	Cube
SAPR-8	5 D_{4d}	Square antiprism
TDD-8	6 D_{2d}	Triangular dodecahedron
JGBF-8	7 D_{2d}	Johnson gyrobifastigium J26
JETBPY-8	8 D_{3h}	Johnson elongated triangular bipyramid J14
JBTPR-8	9 C_{2v}	Biaugmented trigonal prism J50
BTPR-8	10 C_{2v}	Biaugmented trigonal prism
JSD-8	11 D_{2d}	Snub diphenoid J84
TT-8	12 T_d	Triakis tetrahedron
ETBPY-8	13 D_{3h}	Elongated trigonal bipyrami

Structure [ML8]	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8	ETBPY-8
ABOXIY	32.505	22.684	15.372	11.190	2.043	1.701	14.264	29.538	2.007	1.155	4.144	11.903	25.136

Table S4 Continuous shape measures calculation for Tb1 in **S-Tb-2**. The lowest CShMs value is marked in red.

OP-8	1 D_{8h}	Octagon
HPY-8	2 C_{7v}	Heptagonal pyramid
HBPY-8	3 D_{6h}	Hexagonal bipyramid
CU-8	4 O_h	Cube
SAPR-8	5 D_{4d}	Square antiprism
TDD-8	6 D_{2d}	Triangular dodecahedron
JGBF-8	7 D_{2d}	Johnson gyrobifastigium J26
JETBPY-8	8 D_{3h}	Johnson elongated triangular bipyramid J14
JBTPR-8	9 C_{2v}	Biaugmented trigonal prism J50
BTPR-8	10 C_{2v}	Biaugmented trigonal prism
JSD-8	11 D_{2d}	Snub diphenoid J84
TT-8	12 T_d	Triakis tetrahedron
ETBPY-8	13 D_{3h}	Elongated trigonal bipyrami

Structure [ML8]	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8	ETBPY-8
ABOXIY	28.710	21.220	14.276	11.135	2.181	2.569	11.788	26.768	2.846	**1.863**	4.151	11.929	23.206

Table S5 Continuous shape measures calculation for Tb2 in **S-Tb-2**. The lowest CShMs value is marked in red.

OP-8	1 D_{8h}	Octagon
HPY-8	2 C_{7v}	Heptagonal pyramid
HBPY-8	3 D_{6h}	Hexagonal bipyramid
CU-8	4 O_h	Cube
SAPR-8	5 D_{4d}	Square antiprism
TDD-8	6 D_{2d}	Triangular dodecahedron
JGBF-8	7 D_{2d}	Johnson gyrobifastigium J26
JETBPY-8	8 D_{3h}	Johnson elongated triangular bipyramid J14
JBTPR-8	9 C_{2v}	Biaugmented trigonal prism J50
BTPR-8	10 C_{2v}	Biaugmented trigonal prism
JSD-8	11 D_{2d}	Snub diphenoid J84
TT-8	12 T_d	Triakis tetrahedron
ETBPY-8	13 D_{3h}	Elongated trigonal bipyrami

Structure [ML8]	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	TDD-8	JGBF-8	JETBPY-8	JBTPR-8	BTPR-8	JSD-8	TT-8	ETBPY-8
ABOXIY	29.259	22.584	16.773	10.964	0.735	1.689	14.719	27.190	2.628	2.070	4.076	11.655	22.940

Table S6 Calculated dipole moments of mononuclear **S-Tb-1** and dinuclear **S-Tb-2**.

Compound	**S-Tb-1**	**S-Tb-2**
μ_{total} (D)	7.0623	1.8504
X	2.2261	–0.0737
Y	–6.7007	1.8419
Z	–0.1479	0.1603