Supporting Information

Temperature dependent 3D structures of lanthanide coordination polymers based on dicarboxylate mixed ligands

Kittipong Chainok,[a]* Nutcha Ponjan,[a] Chatphorn Theppitak,[a] Phailyn Khemthong,[b] Filip Kielar,[b] Winya Dungkaew,[c] Yan Zhou[d] and Stuart R. Batten[e]

[a]*Materials and Textile Technology, Faculty of Science and Technology, Thammasat University, Khlong Luang, Pathum Thani 12121, Thailand, E-mail: kc@tu.ac.th; Fax: +66 2 654 4548; Tel: +66 86 339 5079*

[b]*Department of Chemistry, Faculty of Science, Naresuan University, Muang, Phitsanulok 65000, Thailand*

[c]*Department of Chemistry, Faculty of Science, Mahasarakham University, Kantharawichai, Maha Sarakham 44150, Thailand*

[d]*Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR China*

[e]*School of Chemistry, Monash University, Clayton, Victoria 3800, Australia*

Table S1. Selected bond lengths and bond angles for **1** and **2**.

	$\mathbf{1}_{Sm}$	$\mathbf{2}_{Tb}$
Ln1−O1	2.5530(16)	2.516(4)
Ln1−O2	2.5373(15)	2.510(3)
Ln1−O3	2.4349(16)	2.343(4)
Ln1−O3^{i}	2.7448(16)	2.906(4)
Ln1−O4^{i}	2.4640(16)	2.398(4)
Ln1−O5^{ii}	2.4765(15)	2.426(3)
Ln1−O6^{iii}	2.4572(16)	2.379(4)
Ln1−O7	2.4552(17)	2.408(4)
Ln1−O8	2.4293(19)	2.396(4)

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x, −y+2, −z+1; (iii) x, y−1, z.

Table S2. Selected bond lengths and bond angles for **3-6**.

	$\mathbf{3}_{Sm}$	$\mathbf{4}_{Eu}$	$\mathbf{5}_{Tb}$	$\mathbf{6}_{Er}$
Ln1−O1	2.465(3)	2.454(3)	2.432(6)	2.391(4)
Ln1−O2	2.534(3)	2.523(2)	2.502(5)	2.484(3)
Ln1−O5	2.408(3)	2.394(3)	2.372(6)	2.336(3)
Ln1−O7^{i}	2.627(3)	2.630(3)	2.626(6)	2.621(3)
Ln1−O8^{i}	2.487(4)	2.477(3)	2.458(6)	2.409(4)
Ln1−O9	2.378(3)	2.365(2)	2.340(5)	2.305(3)
Ln1−O12^{ii}	2.381(3)	2.369(3)	2.330(5)	2.286(3)
Ln1−O13	2.490(4)	2.475(3)	2.446(7)	2.430(4)
Ln1−O14	2.26(13)	2.76(7)	2.52(16)	2.397(4)
Ln2−O3^{iii}	2.477(4)	2.464(3)	2.433(6)	2.413(3)
Ln2−O4^{iii}	2.476(3)	2.465(3)	2.447(6)	2.420(3)
Ln2−O6	2.492(3)	2.481(3)	2.453(6)	2.286(3)
Ln2−O7^{i}	2.356(3)	2.343(2)	2.318(5)	2.279(3)
Ln2−O10	2.378(3)	2.356(2)	2.321(5)	2.321(4)
Ln2−O11^{ii}	2.396(3)	2.384(3)	2.358(6)	2.377(4)
Ln2−O12^{ii}	2.459(4)	2.447(3)	2.409(6)	2.854(4)
Ln2−O15	2.788(3)	2.791(3)	2.805(6)	2.416(4)
Ln2−O16	2.494(4)	2.484(3)	2.463(7)	2.349(4)

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1; (ii) −*x*+1, *y*+1/2, −*z*+2; (iii) *x*−1, *y*, *z*+1.

Table S3. Selected bond lengths and bond angles for **7-10**.

	$\mathbf{7}_{Sm}$	$\mathbf{8}_{Eu}$	$\mathbf{9}_{Tb}$	$\mathbf{10}_{Er}$
Ln1−O1	2.431(6)	2.438(3)	2.414(2)	2.384(2)
Ln1−O1^{i}	2.510(5)	2.490(3)	2.464(2)	2.424(2)
Ln1−O2^{ii}	2.517(6)	2.505(3)	2.488(2)	2.476(2)
Ln1−O2^{i}	2.677(5)	2.662(3)	2.640(2)	2.598(2)
Ln1−O3	2.270(6)	2.263(3)	2.239(2)	2.205(2)
Ln1−O4^{iii}	2.340(5)	2.332(3)	2.299(2)	2.263(2)
Ln1−O5^{iv}	2.364(6)	2.355(3)	2.333(3)	2.302(2)
Ln1−O6^{v}	2.350(6)	2.337(3)	2.309(2)	2.274(2)

Symmetry codes: (i) −x+3/2, y+1/2, z; (ii) x, y+1, z; (iii) −x+1, −y+2, −z+1; (iv) −x+1, y+1/2, −z+3/2; (v) x+1/2, y, −z+3/2

Table S4. Selected bond lengths and bond angles for **11-14**.

	$\mathbf{11}_{Sm}$	$\mathbf{12}_{Gd}$	$\mathbf{13}_{Tb}$	$\mathbf{14}_{Dy}$
Ln1−O1	2.320(2)	2.297(2)	2.278(3)	2.269(2)
Ln1−O2^{i}	2.394(2)	2.363(2)	2.342(3)	2.333(2)
Ln1−O3^{ii}	2.378(2)	2.354(2)	2.338(3)	2.327(2)
Ln1−O4^{iii}	2.339(2)	2.313(2)	2.291(3)	2.283(2)
Ln1−O5	2.465(2)	2.443(2)	2.432(3)	2.423(2)
Ln1−O6^{iv}	2.498(2)	2.472(2)	2.463(3)	2.448(2)
Ln1−O7	2.516(3)	2.492(2)	2.476(3)	2.470(2)
Ln1−O8	2.513(3)	2.481(2)	2.469(3)	2.454(2)

Symmetry codes: (i) −x, −y+1, −z+1; (ii) −x+1, y+1/2, −z+3/2; (iii) x, −y+1/2, z+1/2; (iv) −x, −y+1, −z+2.

Table S5 Hydrogen-bond geometry (Å, °) for **1** and **2**.

D−H···*A*	*D*−H		H···*A*		*D*···*A*		*D*−H···*A*	
	$\mathbf{1}_{Sm}$	$\mathbf{2}_{Tb}$	$\mathbf{1}_{Sm}$	$\mathbf{2}_{Tb}$	$\mathbf{1}_{Sm}$	$\mathbf{2}_{Tb}$	$\mathbf{1}_{Sm}$	$\mathbf{2}_{Tb}$
O7−H7*A*···O2^{i}	0.83(1)	0.84(1)	1.99(1)	1.99(2)	2.821(2)	2.815(5)	176(3)	167(6)
O7−H7*B*···O9	0.84(1)	0.84(1)	1.99(2)	2.04(3)	2.781(2)	2.792(5)	158(3)	149(5)
O8−H8*A*···O1^{ii}	0.83(1)	0.84(1)	1.93(1)	1.93(2)	2.726(2)	2.749(6)	162(3)	165(6)
O8−H8*B*···O9^{iii}	0.83(1)	0.84(1)	2.02(1)	2.01(1)	2.832(3)	2.844(6)	168(4)	175(7)
O10−H10···O11	0.82(1)	0.82(1)	1.76(1)	1.77(2)	2.579(3)	2.584(6)	176(4)	170(8)
O11−H11*A*···O2^{i}	0.84(1)	0.84(1)	2.06(1)	2.06(1)	2.889(3)	2.900(6)	171(3)	175(8)
O11−H11*B*···O5^{i}	0.84(1)	0.83(1)	2.03(1)	2.10(2)	2.867(3)	2.917(6)	177(4)	169(5)

Symmetry codes: (i) −x, −y+1, −z+1; (ii) −x+1, −y+1, −z+1; (iii) −x, −y+1, −z+2.

Table S6 Hydrogen-bond geometry (Å, °) for **3-6**.

D–H···*A*	*D*–H		H···*A*		*D*···*A*		*D*–H···*A*	
	3$_{Sm}$	**4**$_{Eu}$	**3**$_{Sm}$	**4**$_{Eu}$	**3**$_{Sm}$	**4**$_{Eu}$	**3**$_{Sm}$	**4**$_{Eu}$
O13–H13*A*···O17	0.83(1)	0.83(1)	1.95(3)	1.93(2)	2.734(6)	2.744(5)	157(7)	167(5)
O14–H14*A*···O3^{i}	0.84(1)	0.84(1)	1.88(3)	1.93(4)	2.706(5)	2.702(4)	166(8)	151(7)
O14–H14*B*···O17	0.84(2)	0.84(1)	2.15(5)	2.18(3)	2.900(6)	2.902(5)	150(8)	145(5)
O15–H15*A*···O11^{iii}	0.84(2)	0.84(1)	2.21(11)	2.03(4)	2.819(6)	2.818(5)	129(12)	156(8)
O15–H15*B*···O3^{iv}	0.84(1)	0.83(1)	2.52(6)	2.78(6)	3.178(6)	3.184(4)	137(8)	112(5)
O16–H16*A*···O2^{iii}	0.83(1)	0.82(1)	1.92(2)	1.93(2)	2.743(5)	2.741(4)	170(5)	169(4)
O16–H16*B*···O18	0.83(1)	0.83(1)	1.85(2)	1.86(2)	2.683(6)	2.677(5)	175(5)	171(6)
O17–H17*A*···O8^{v}	0.84(1)	0.84(1)	2.24(6)	2.15(3)	2.889(6)	2.882(5)	134(7)	146(5)
O17–H17*B*···O4^{vi}	0.84(1)	0.83(1)	2.52(6)	2.56(5)	3.120(6)	3.121(5)	130(7)	125(5)
O17–H17*B*···O10^{vii}	0.84(1)	0.83(1)	2.39(5)	2.36(3)	3.124(6)	3.128(5)	147(8)	152(5)
O18–H18*A*···O11^{iii}	0.84(1)	0.83(1)	2.13(3)	2.14(2)	2.930(7)	2.938(5)	160(8)	162(5)
O18–H18*B*···O1^{viii}	0.84(1)	0.83(1)	1.97(2)	1.97(2)	2.789(6)	2.783(5)	168(7)	166(5)
D–H···*A*	*D*–H		H···*A*		*D*···*A*		*D*–H···*A*	
	5$_{Tb}$	**6**$_{Er}$	**5**$_{Tb}$	**6**$_{Er}$	**5**$_{Tb}$	**6**$_{Er}$	**5**$_{Tb}$	**6**$_{Er}$
O13–H13*A*···O17	0.83(2)	0.84(2)	1.94(3)	1.95(3)	2.744(10)	2.771(7)	163(8)	164(9)
O14–H14*A*···O3^{i}	0.84(2)	0.84(1)	1.88(2)	1.90(3)	2.711(9)	2.713(6)	170(8)	164(10)
O14–H14*B*···O17	0.84(2)	0.84(1)	2.19(12)	2.16(4)	2.880(11)	2.881(6)	139(16)	145(7)
O15–H15*A*···O11^{iii}	0.84(2)	0.84(1)	2.10(7)	2.14(6)	2.843(9)	2.883(6)	147(11)	147(9)
O15–H15*B*···O3^{iv}	0.84(2)	0.84(1)	2.52(10)	2.56(7)	3.175(10)	3.188(6)	135(12)	133(8)
O16–H16*A*···O2^{iii}	0.83(2)	0.84(1)	1.98(4)	1.92(2)	2.747(8)	2.737(5)	153(9)	164(5)
O16–H16*B*···O18	0.84(2)	0.84(1)	1.88(6)	1.86(2)	2.671(10)	2.689(6)	156(14)	167(7)
O17–H17*A*···O8^{v}	0.84(2)	0.84(1)	2.10(4)	2.16(4)	2.892(10)	2.893(6)	157(8)	147(7)
O17–H17*B*···O4^{vi}	0.84(2)	0.83(1)	2.53(8)	2.44(5)	3.109(10)	3.079(6)	128(8)	134(6)
O17–H17*B*···O10^{vii}	0.84(2)	0.83(1)	2.42(5)	2.43(4)	3.136(10)	3.163(6)	144(7)	148(6)
O18–H18*A*···O11^{iii}	0.84(2)	0.84(1)	2.17(8)	2.15(3)	2.941(11)	2.940(6)	153(15)	157(8)
O18–H18*B*···O1^{viii}	0.84(2)	0.84(1)	1.94(3)	1.94(2)	2.768(10)	2.773(7)	171(13)	174(8)

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*−1, *y*, *z*+1; (iii) *x*−1, *y*, *z*; (iv) −*x*+1, *y*−1/2, −*z*+1; (v) *x*+1, *y*, *z*; (vi) −*x*+2, *y*+1/2, −*z*+1; (vii) −*x*+1, *y*+1/2, −*z*+2; (viii) −*x*, *y*−1/2, −*z*+1.

Table S7 Hydrogen-bond geometry (Å, °) for **7-10**.

D–H···*A*	*D*–H		H···*A*		*D*···*A*		*D*–H···*A*	
	7$_{Sm}$	**8**$_{Eu}$	**7**$_{Sm}$	**8**$_{Eu}$	**7**$_{Sm}$	**8**$_{Eu}$	**7**$_{Sm}$	**8**$_{Eu}$
C2–H2···O3	0.93	0.93	2.40	2.41	3.204(11)	3.204(5)	144	144
D–H···*A*	*D*–H		H···*A*		*D*···*A*		*D*–H···*A*	
	9$_{Tb}$	**10**$_{Er}$	**9**$_{Tb}$	**10**$_{Er}$	**9**$_{Tb}$	**10**$_{Er}$	**9**$_{Tb}$	**10**$_{Er}$
C2–H2···O3	0.93	0.93	2.39	2.36	3.184(5)	3.144(4)	143	141

Table S8 Hydrogen-bond geometry (Å, °) for **11-14**.

D–H···*A*	*D*–H		H···*A*		*D*···*A*		*D*–H···*A*	
	11$_{Sm}$	**12**$_{Gd}$	**11**$_{Sm}$	**12**$_{Gd}$	**11**$_{Sm}$	**12**$_{Gd}$	**11**$_{Sm}$	**12**$_{Gd}$
O7–H7*A*···O9	0.83(1)	0.83(1)	2.34(2)	2.34(2)	3.147(9)	3.165(8)	164(5)	169(5)
O7–H7*B*···O6^{vii}	0.84(1)	0.84(1)	1.98(2)	1.99(1)	2.809(4)	2.814(3)	171(6)	168(4)
O8–H8*A*···O5^{viii}	0.84(1)	0.84(1)	1.99(2)	1.98(1)	2.808(4)	2.807(3)	165(5)	171(4)
D–H···*A*	*D*–H		H···*A*		*D*···*A*		*D*–H···*A*	
	13$_{Tb}$	**14**$_{Dy}$	**13**$_{Tb}$	**14**$_{Dy}$	**13**$_{Tb}$	**14**$_{Dy}$	**13**$_{Tb}$	**14**$_{Dy}$
O7–H7*A*···O9	0.84(1)	0.84(1)	2.31(2)	2.33(2)	3.136(9)	3.155(6)	170(5)	169(5)
O7–H7*B*···O6^{vii}	0.84(1)	0.84(1)	1.99(1)	1.99(1)	2.821(5)	2.825(3)	171(4)	169(4)
O8–H8*A*···O5^{viii}	0.84(1)	0.84(1)	1.98(1)	1.99(1)	2.815(5)	2.821(3)	172(6)	173(4)

Symmetry codes: (vii) $x, y, z-1$; (viii) $-x+1, -y+1, -z+2$.

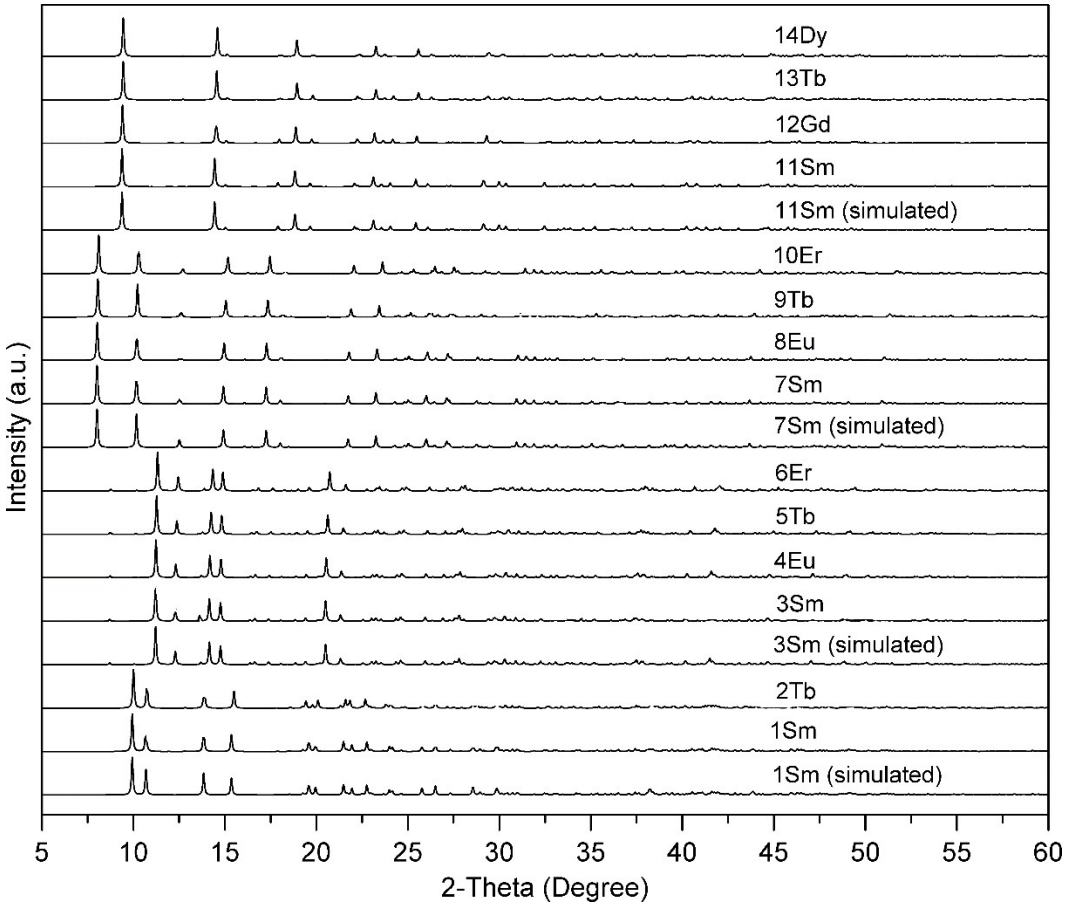

Fig. S1 PXRD patterns for **1-14**.

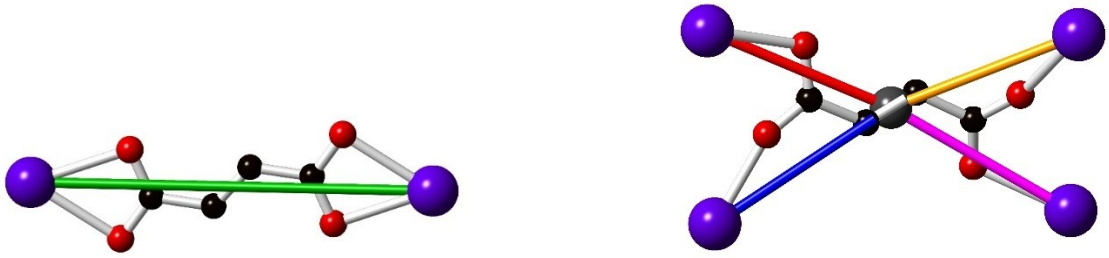

Fig. S2 The simplified 2- and 3-connected node of the fum ligand in **2**.

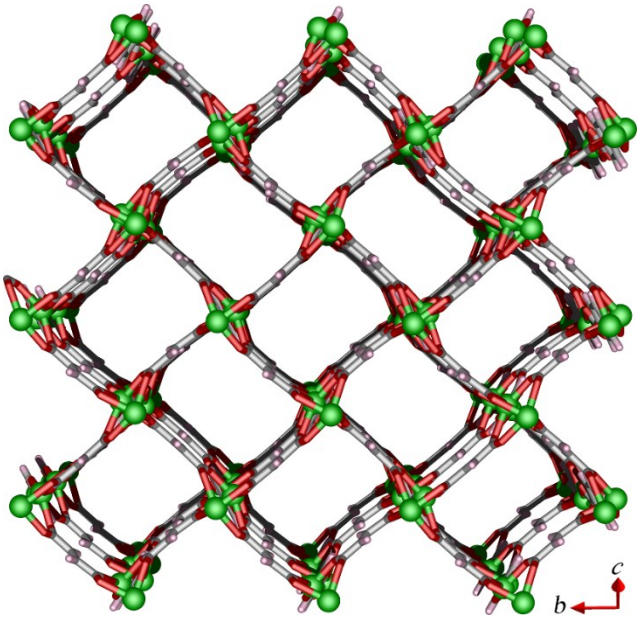

Fig. S3 Prospective views of the single 3D nets in the *bc* plane in **5**.

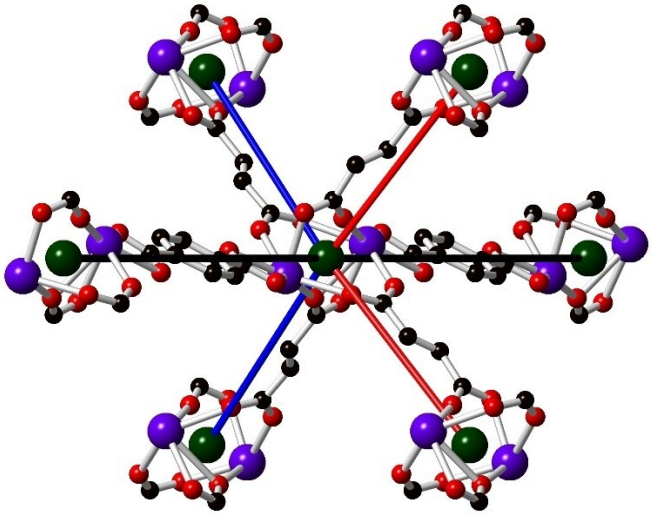

Fig. S4 The simplified 6-connected node in **5**.

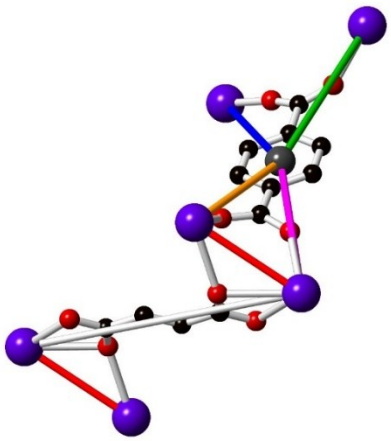

Fig. S5 The simplified 6-connected node in **9**.

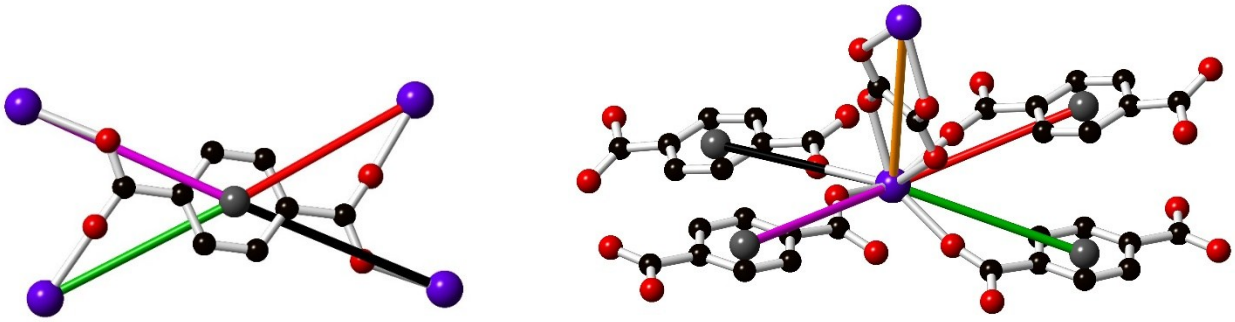

Fig. S6 The simplified 4-connected node of the tp ligand (left) and 5-connected node of the metals in **13**.

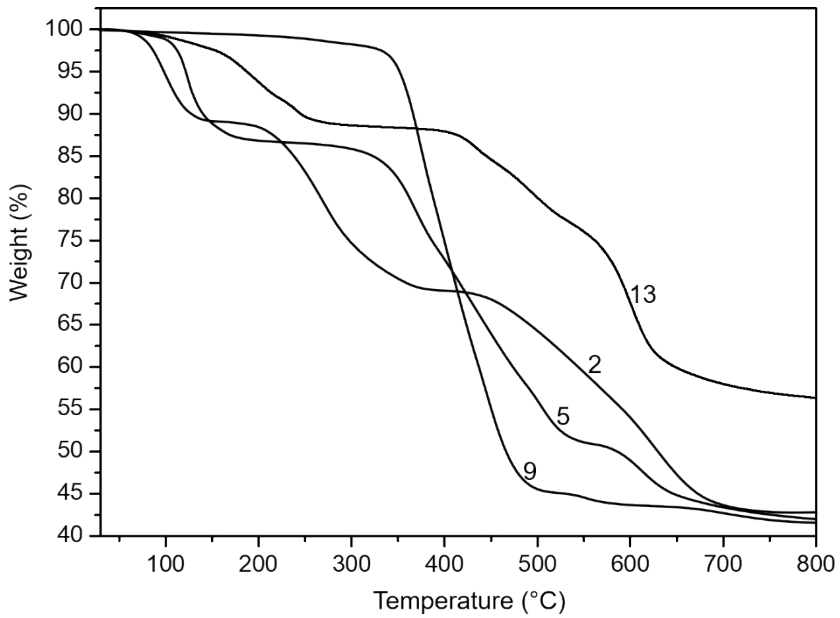

Fig. S7 TG curves for Tb based compounds **2**, **5**, **9** and **13**.

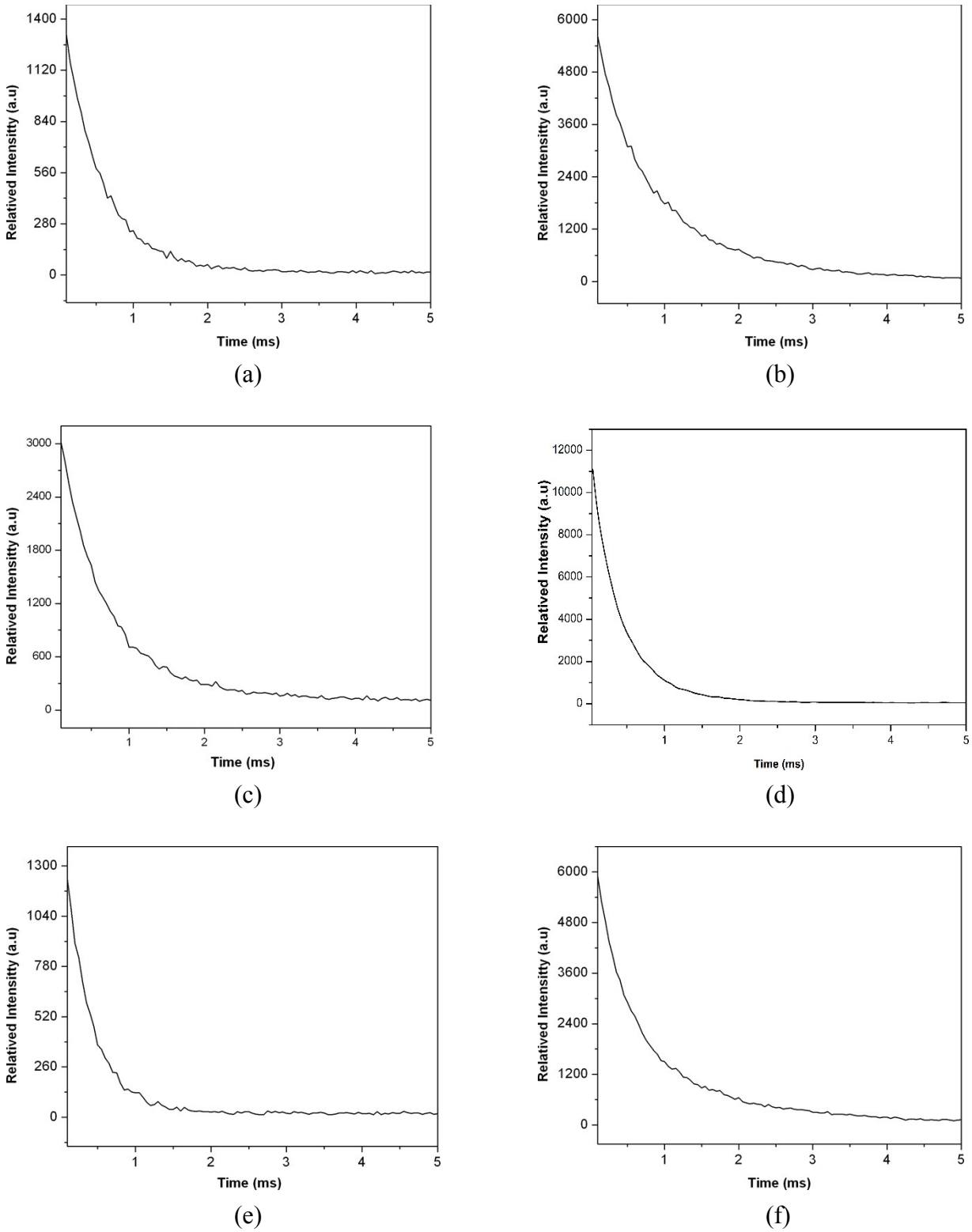

Fig. S8 The emission intensity decay curves for the Tb-based compounds (a) **2**, (b) **5**, (c) **9** and (d) **13**, and the Eu-based compounds (e) **4** and (f) **8**.