Supporting Information

K^{I}-induced Synthesis of Highly Connected 3D K^{I}-Ln^{III} Heterobimetallic MOFs: Temperature-dependent Structure and Physical properties

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Thermogravimetric analyses.

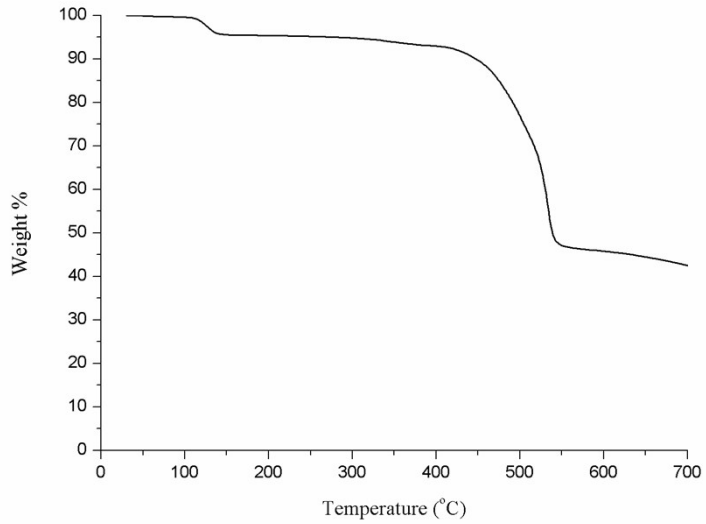

Figure S1. TGA of **1**. Measurements were performed on NETZSCH TG 209F1 Iris. Conditions: temperature ramp from 25 ˚C to 700 ˚C at 10 ˚C/min under flow of air gas.

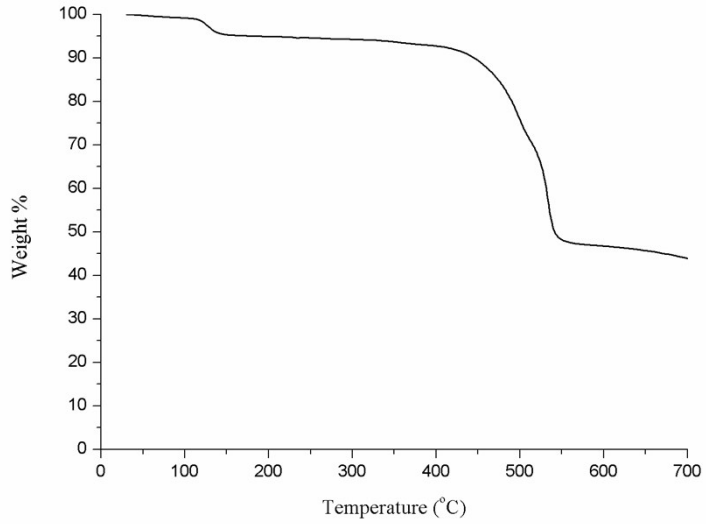

Figure S2. TGA of **2**. Measurements were performed on NETZSCH TG 209F1 Iris. Conditions: temperature ramp from 25 ˚C to 700 ˚C at 10 ˚C/min under flow of air gas.

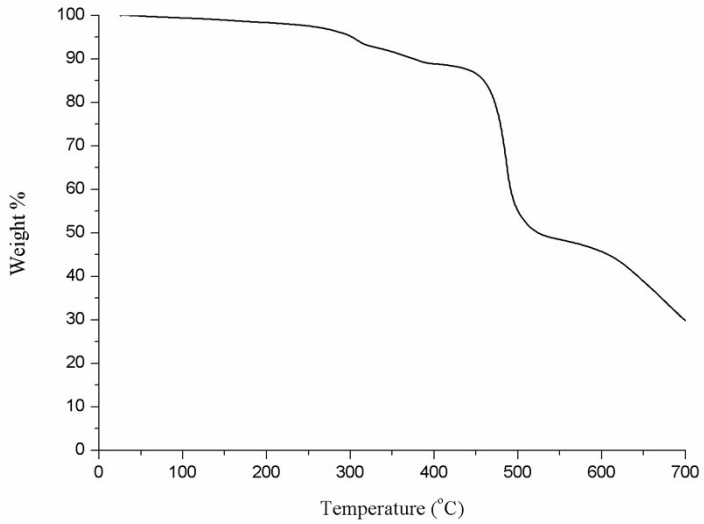

Figure S3. TGA of **3**. Measurements were performed on NETZSCH TG 209F1 Iris. Conditions: temperature ramp from 25 ˚C to 700 ˚C at 10 ˚C/min under flow of air gas.

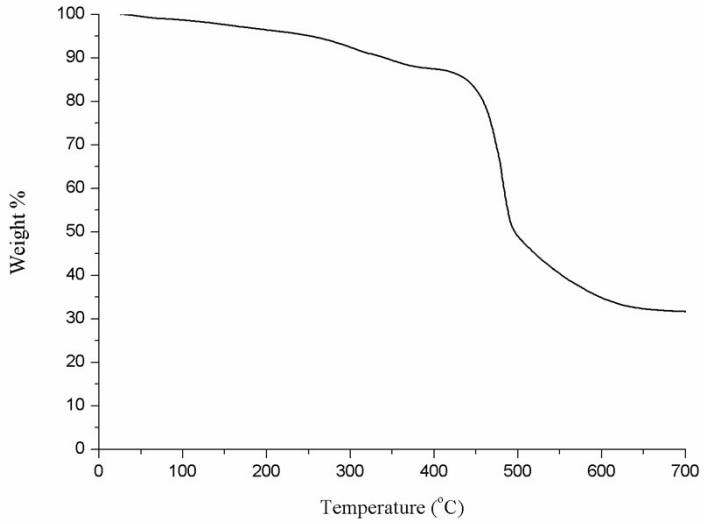

Figure S4. TGA of **4**. Measurements were performed on NETZSCH TG 209F1 Iris. Conditions: temperature ramp from 25 ˚C to 700 ˚C at 10 ˚C/min under flow of air gas.

General Procedure for EDX Experiment. Air-dried, ethanol-activated samples (ca. 5 mg) were examined using a Carl Zeiss-ZEISS Ultra 55 SEM apparatus equipped an EDAX Genesis system with a conventional Si(Li) detector with light-element capabilities. A typical setup consisted of a 20kV accelerating voltage, a 35 degree takeoff angle, and a working distance of 8.5 μm. The duration of the EDX scans on individual samples was ca. 30s.

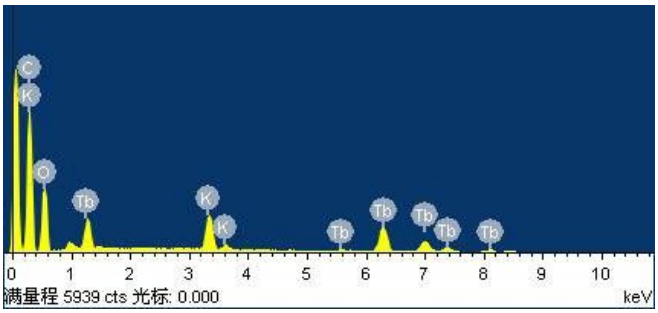

Figure S5. SEM/EDX of **1**. SEM apparatus.
Entergy-dispersive spectrometry (EDS) gives the K/Tb 1:1.2 molar ratio in **1** as (calcd K/Tb 1:1)

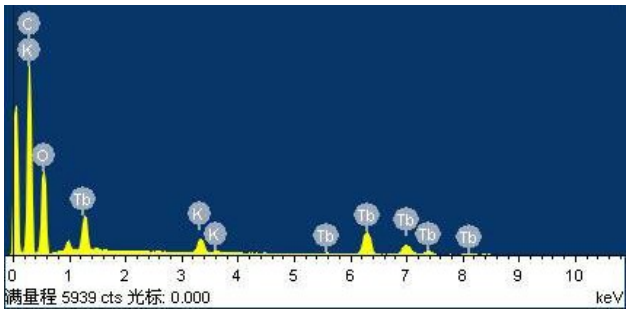

Figure S6. SEM/EDX of **3**. SEM apparatus.
Entergy-dispersive spectrometry (EDS) gives the K/Tb 1:3.1 molar ratio in **3** as (calcd K/Tb 1:3)

Powder X-Ray Diffraction. X-ray powder diffraction measurements were measured on a X-pert diffractometer or Rigaku D/M-2200T automated diffractometer for Cu Kα radiation (λ=1.54056 Å) with a scan speed of 2˚ min^{-1} in 2θ range of 5-50˚.

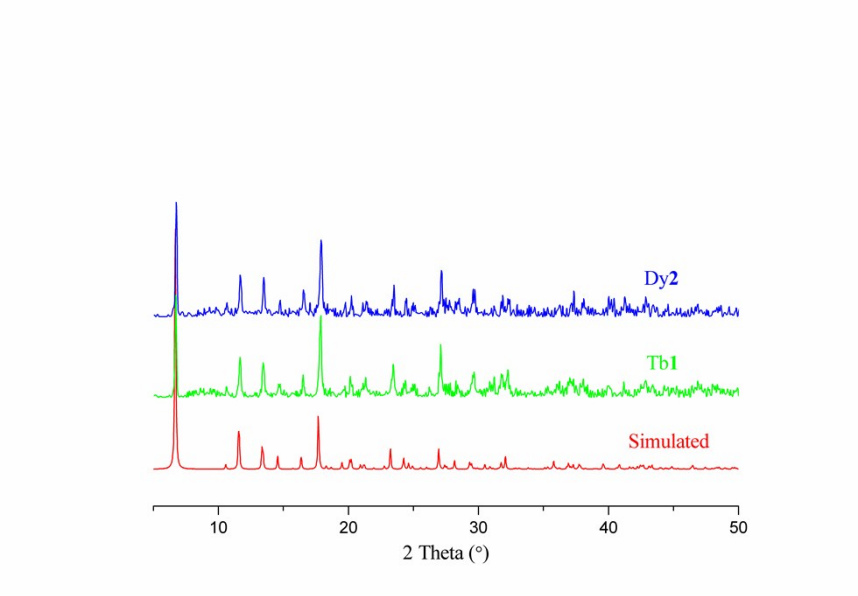

Figure S7. PXRD patterns for activated **1** and **2.**

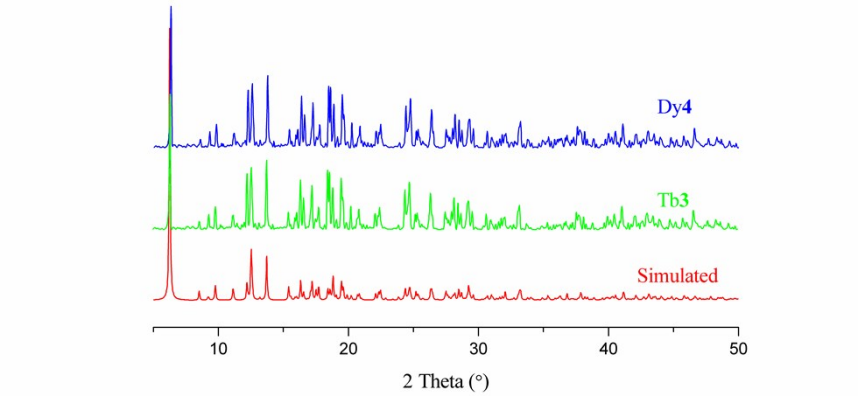

Figure S8. PXRD patterns for activated **1** and **2.**

FT-IR analyses. The FT-IR samples were prepared as KBr pellets, and spectra were obtained in the range of 4000-500cm^{-1} on a Nicolet 6700 spectrometer.

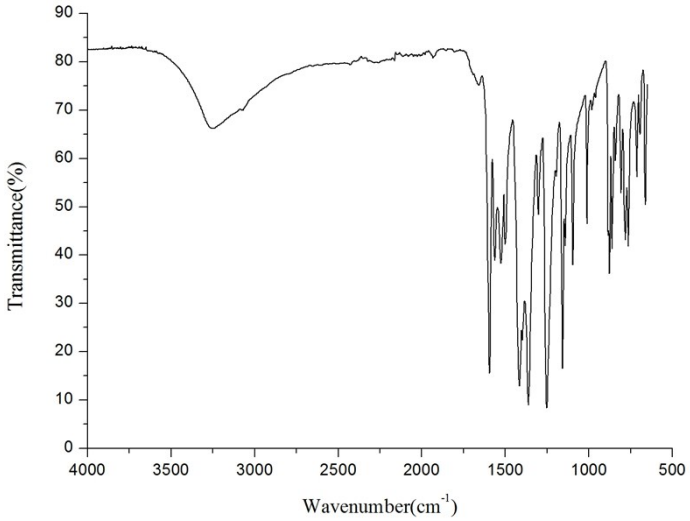

Figure S9. IR spectrum of complex **1.**

IR (KBr, cm^{-1}): 3067(w), 1657(w), 1594(s), 1563(w), 1526(w), 1501(w), 1415(s), 1362(s), 1302(w), 1241(s), 1157(s), 1141(w), 1095(m), 1012(m), 876(m), 862(m), 841(w), 807(m), 781(m), 764(w), 712(m), 693(w), 662(s).

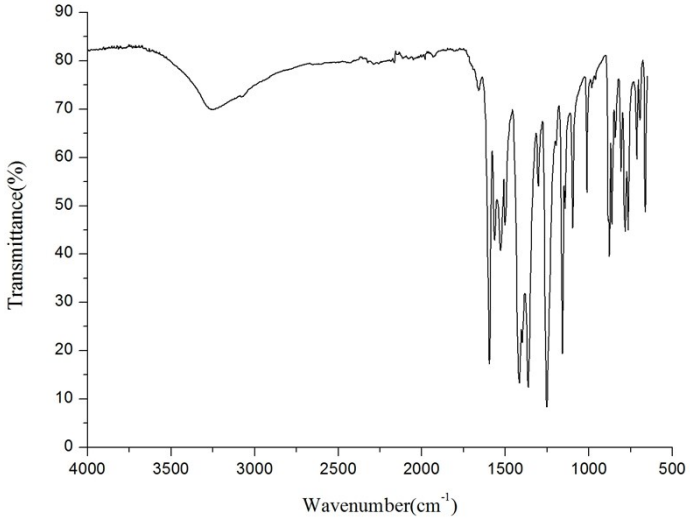

Figure S10. IR spectrum of complex **2.**

IR (KBr, cm^{-1}): 3064(w), 1659(w), 1595(s), 1564(w), 1528(w), 1502(w), 1416(s), 1363(s), 1302(w), 1251(s), 1157(s), 1141(w), 1096(m), 1011(m), 877(m), 862(m), 841(w), 807(m), 782(m), 764(m), 712(m), 693(w), 662(s).

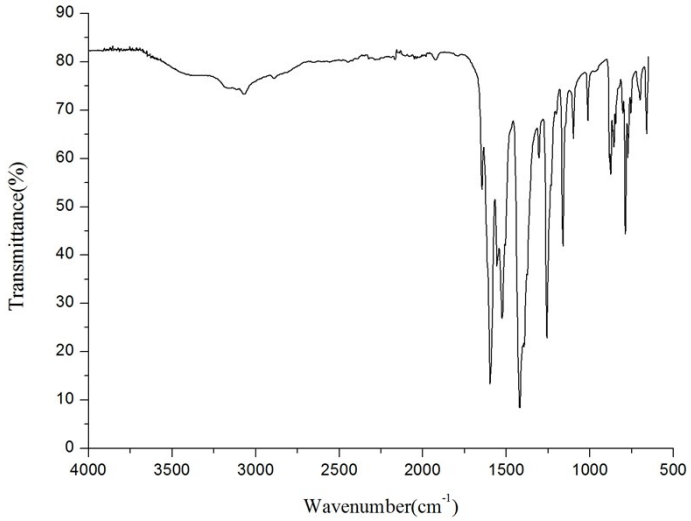

Figure S11. IR spectrum of complex **3.**
IR (KBr, cm^{-1}): 3068(w), 1654(w), 1597(s), 1557(w), 1525(m), 1419(s), 1304(w), 1257(s), 1160(s), 1098(w), 1012(w), 875(m), 856(w), 787(s), 772(w), 753(w), 699(w), 660(m).

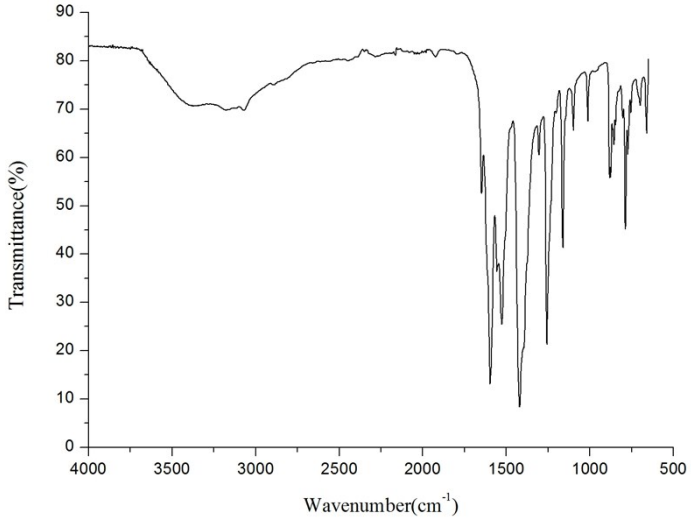

Figure S12. IR spectrum of complex **4.**
IR (KBr, cm^{-1}): 3073(w), 1647(w), 1597(s), 1557(w), 1526(m), 1422(s), 1304(w), 1257(s), 1161(s), 1098(w), 1012(w), 875(m), 847(w), 787(s), 772(w), 754(w), 698(w), 660(m).

Table S1. Crystal Data and Structure Refinement Summary for compounds 1−4.

complex	1	2	3	4
empirical formula	$C_{28}H_{26}O_{15}KTb$	$C_{28}H_{26}O_{15}KDy$	$C_{59}H_{39}O_{28}KTb_3$	$C_{59}H_{39}O_{28}KDy_3$
formula weight	800.53	804.11	1712.91	1720.91
T (K)	296(2)	296(2)	296(2)	296(2)
crystal system	Tetragonal	Tetragonal	Orthorhombic	Orthorhombic
space group	*P4/nnc*	*P4/nnc*	*Pnma*	*Pnma*
a (Å)	15.513(2)	15.322(2)	20.15(5)	19.100(3)
b (Å)	15.513(2)	15.322(2)	30.14(7)	28.260(4)
c (Å)	26.445(4)	26.327(4)	11.69(3)	11.1446(19)
a (deg)	90	90	90	90
β(deg)	90	90	90	90
γ(deg)	90	90	90	90
V ($Å^3$)	6364.1(19)	6180.6(19)	7100(30)	6015.5(16)
Z	8	8	4	4
D calcd (g cm^{-3})	1.621	1.664	1.611	1.901
μ/mm^{-1}	2.418	2.593	3.091	3.848
F (000)	3056	3050.4	3308	3332
GOF	0.953	1.059	1.001	1.048
R1 [I > 2σ(I)] [a]	0.0719	0.0822	0.0609	0.0587
ωR_2 (all data) [b]	0.2427	0.3021	0.1690	0.1544
Data/restraints/parameters	3613 / 9 / 203	2815 / 3 / 212	6541 / 3 / 426	7072 / 9 / 424
CCDC number	1421853	1421854	1421855	1421856

[a] $R_1=\sum||F_0|-|F_c||/\sum|F_0|$. [b] $_wR_2=\{\sum[w(F_0^2-F_c^2)^2]/\sum(F_0^2)^2\}^1$

Crystal structures

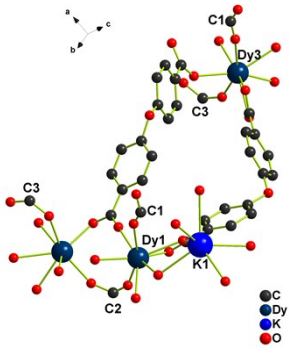

Figure S13. The coordination environment in **4** (hydrogen omitted for clarity).

Table S2. Selected bond lengths (Å) for complexes 1 and 2

1		**2**	
Tb(1)-O(4)#2	2.339(6)	Dy(1)-O(5)#2	2.314(11)
Tb(1)-O(4)#3	2.339(6)	Dy(1)-O(5)#3	2.314(11)
Tb(1)-O(5)#4	2.354(5)	Dy(1)-O(4)#4	2.324(12)
Tb(1)-O(5)#5	2.354(5)	Dy(1)-O(4)#5	2.324(12)
Tb(1)-O(1)#6	2.439(6)	Dy(1)-O(1)	2.412(13)
Tb(1)-O(1)	2.439(6)	Dy(1)-O(1)#6	2.412(13)
Tb(1)-O(2)#6	2.461(7)	Dy(1)-O(2)	2.414(13)
Tb(1)-O(2)	2.461(7)	Dy(1)-O(2)#6	2.414(13)
K(1)-O(5)#8	2.793(6)	K(1)-O(5)#8	2.763(12)
K(1)-O(5)#9	2.793(6)	K(1)-O(5)#2	2.763(12)
K(1)-O(5)#10	2.793(6)	K(1)-O(5)#9	2.763(12)
K(1)-O(5)#11	2.793(6)	K(1)-O(5)#10	2.763(12)
K(1)-O(5)#12	2.793(6)	K(1)-O(5)#11	2.763(12)
K(1)-O(5)	2.793(6)	K(1)-O(5)#3	2.763(12)
K(1)-O(5)#13	2.793(6)	K(1)-O(5)#4	2.763(12)
K(1)-O(5)#14	2.793(6)	K(1)-O(5)#5	2.763(12)
K(2)-O(1)#17	2.570(7)	K(2)-O(1W)#15	2.74(4)
K(2)-O(1)	2.570(7)	K(2)-O(1W)#15	2.74(4)
K(2)-O(1W)#18	2.98(6)	K(2)-O(4)#4	2.920(19)
K(2)-O(1W)	2.98(6)	K(2)-O(4)#3	2.920(19)
K(2)-O(4)#4	2.960(9)	K(2)-O(1)#14	2.555(16)
K(2)-O(4)#3	2.960(9)	K(2)-O(1)#14	2.555(16)

Table S3. Selected bond lengths (Å) for complexes 3 and 4

3		**4**	
K(1)-O(13)	2.819(9)	K(1)-O(10)#8	2.677(7)
K(1)-O(13)#2	2.819(9)	K(1)-O(10)#9	2.677(7)
K(1)-O(15)#3	2.891(11)	K(1)-O(7)	2.736(12)
K(1)-O(15)#1	2.891(11)	K(1)-O(7)#2	2.736(12)
K(1)-O(7)	2.985(9)	K(1)-O(16)#10	2.837(7)
K(1)-O(7)#2	2.985(9)	K(1)-O(16)#5	2.837(7)
K(1)-O(6)#4	3.212(15)	K(1)-O(6)#11	3.046(10)
K(1)-O(4)	3.236(14)	K(1)-O(4)#12	3.096(11)
Tb(1)-O(11)#8	2.423(11)	Dy(1)-O(3)	2.242(10)
Tb(1)-O(11)#10	2.423(11)	Dy(1)-O(2)	2.285(11)
Tb(1)-O(16)#11	2.458(12)	Dy(1)-O(12)#2	2.297(11)
Tb(1)-O(16)#9	2.458(12)	Dy(1)-O(12)	2.297(11)
Tb(1)-O(15)#9	2.617(10)	Dy(1)-O(8)	2.311(9)
Tb(1)-O(15)#11	2.617(10)	Dy(1)-O(8)#2	2.311(9)
Tb(1)-O(2)	2.421(13)	Dy(1)-O(7)#2	2.489(10)
Tb(1)-O(3)	2.373(12)	Dy(1)-O(7)	2.489(10)
Tb(2)-O(10)#8	2.431(10)	Dy(2)-O(4)	2.264(8)
Tb(2)-O(10)#10	2.431(10)	Dy(2)-O(13)#2	2.268(7)
Tb(2)-O(7)#2	2.558(8)	Dy(2)-O(13)	2.268(7)
Tb(2)-O(8)#2	2.705(8)	Dy(2)-O(5)	2.329(9)
Tb(2)-O(8)	2.705(8)	Dy(2)-O(16)#1	2.404(6)
Tb(2)#-O(10)	2.431(10)	Dy(2)-O(16)#3	2.404(6)
Tb(2)-O(4)	2.425(13)	Dy(2)-O(15)#3	2.552(6)
Tb(2)-O(5)	2.453(11)	Dy(2)-O(15)#1	2.552(6)
Tb(3)-O(6)#4	2.400(12)	Dy(3)-O(6)#1	2.252(10)
Tb(3)-O(1)#13	2.415(13)	Dy(3)-O(1)#5	2.295(9)
Tb(3)-O(8)#14	2.484(8)	Dy(3)-O(15)	2.356(6)
Tb(3)-O(8)#4	2.484(8)	Dy(3)-O(15)#6	2.356(6)
Tb(3)-O(12)#2	2.527(12)	Dy(3)-O(11)	2.380(7)
Tb(3)-O(13)#2	2.592(9)	Dy(3)-O(11)#6	2.380(7)
Tb(3)-O(12)	2.527(12)	Dy(3)-O(10)#6	2.440(6)
Tb(3)-O(13)	2.592(9)	Dy(3)-O(10)	2.440(6)